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► **To cite this version:**

Elodie Mattio, Fabien Robert-Peillard, Catherine Branger, Kinga Puzio, André Margaillan, et al.. 3D-printed flow system for determination of lead in natural waters. *Talanta*, Elsevier, 2017, 168, pp.298-302. 10.1016/j.talanta.2017.03.059 . hal-01499475

**HAL Id: hal-01499475**

**<https://hal-amu.archives-ouvertes.fr/hal-01499475>**

Submitted on 18 Apr 2018

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# 3D-printed flow system for determination of lead in natural waters

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## Abstract

The development of 3D printing in recent years opens up a vast array of possibilities in the field of flow analysis. In the present study, a new 3D-printed flow system has been developed for the selective spectrophotometric determination of lead in natural waters. This system was composed of three 3D-printed units (sample treatment, mixing coil and detection) that might have been assembled without any tubing to form a complete flow system. Lead was determined in a two-step procedure. A preconcentration of lead was first carried out on TrisKem Pb Resin located in a 3D-printed column reservoir closed by a tapped screw. This resin showed a high extraction selectivity for lead over many tested potential interfering metals. In a second step, lead was eluted by ammonium oxalate in presence of 4-(2-pyridylazo)-resorcinol (PAR), and spectrophotometrically detected at 520 nm. The optimized flow system has exhibited a linear response from 3 to 120  $\mu\text{g}\cdot\text{L}^{-1}$ . Detection limit, coefficient of variation and sampling rate were evaluated at 2.7  $\mu\text{g}\cdot\text{L}^{-1}$ , 5.4% (n=6) and 4  $\text{sample}\cdot\text{h}^{-1}$ , respectively. This flow system stands out by its fully 3D design, portability and simplicity for low cost analysis of lead in natural waters.

**Keywords:** Lead determination; 3D-printed MPFS system; stereolithography; natural waters

1

## 2 **1. Introduction**

3 Lead is considered as one of the most toxic heavy metals [1] in the light of its environmental  
4 [2] and health [3,4] impacts; it may cause irreversible neurological effects and digestive and  
5 kidney malfunctions. Its presence in the environment and more particularly in water can be  
6 mainly explained by anthropogenic sources like paints, arms and electronic [5] industries  
7 products. For these reasons, the World Health Organization has identified lead as one of the 10  
8 chemicals of major public health concern [6] and has recommended a guideline value of 10  
9  $\mu\text{g.L}^{-1}$  of lead in drinking water. It is therefore necessary to quantify lead by a rapid and efficient  
10 method to avoid toxic consumption.

11 Many methods are already available for lead determination such as spectrophotometry [7],  
12 voltammetry [8,9], graphic furnace atomic absorption spectrometry [10], or inductively coupled  
13 plasma spectroscopy [11,12], but they require costly and sophisticated devices and do not allow  
14 real-time and on-site measurements. In this context, mesofluidic and microfluidic systems can  
15 help to meet these needs thanks to their intrinsic advantages: miniaturization and low energy  
16 consumption, decreased reagents consumption and waste generation. Flow analysis offers many  
17 opportunities [13,14] and Flow Injection Analysis (FIA), Sequential Injection Analysis (SIA)  
18 or MultiSyringe Flow Injection Analysis (MSFIA) based systems have been successfully  
19 applied for the determination of a wide range of substances in environmental matrices. Among  
20 flow analysis system, pulse flow systems using solenoid diaphragm micropumps (MPFS: Multi  
21 Pumping Flow System) present high flexibility, easy configuration and low cost. Another  
22 advantage is that the signal peaks are higher compared to other flow techniques, due to  
23 turbulences created by pump diaphragm strokes, which improve mixing between reagents and  
24 sample [15]. Recently, such MPFS systems were developed for phosphorous [16] or boron [17]  
25 determination in aqueous samples.

1 Several units can be combined to create a flow system in full compliance with the analytical  
2 needs: solid phase extraction for pre-concentration, photo-oxidation or digestion, membrane or  
3 membrane-less separation, detection and many others. To increase versatility and ease of  
4 fabrication of flow systems, 3D printing is increasingly used in flow analysis [18,19]. This  
5 printing technology can be divided into three main categories: Fused Deposition Modeling  
6 (FDM) where a thermoplastic material is heated and extruded from a XYZ positionable nozzle,  
7 Multi Jet Modeling (MJM) which is based on an inkjet head to deposit liquid photopolymer  
8 (plastic resin or casting wax) layer by layer and finally stereolithography (SL) [20] invented in  
9 the 1980s and which is a layer manufacturing process with liquid materials [21] as MJM. SL is  
10 based on a mobile platform which dives in a resin tray, where a laser polymerizes the resin layer  
11 by layer. The most frequently used material is poly(methyl methacrylate) (PMMA) which  
12 allows to decrease fabrication cost and improve resolution [22]. 3D-printing technologies  
13 emergence enables creation of new type of units [23,24] for microfluidic systems which can be  
14 imagined and combined according to the analytical needs.

15 In this paper, the development of a novel 3D-printed multi-pumping flow system for the  
16 determination of lead in natural waters is presented. The system is composed of three 3D-  
17 printed units: a resin column for lead solid phase extraction, a mixing coil and a classical flow  
18 cell for UV-Spectroscopy. The 3 modules are connected to one another by a screw system to  
19 limit tubings between the three units. Lead solid phase extraction is based on a commercial  
20 crown-ethers resin (TrisKem Pb resin) and the chromogenic reagent used for the  
21 spectrophotometric detection of lead is 4-(2-pyridylazo)resorcinol (PAR). The system was  
22 applied to the determination of lead in real river water samples.

23

## 24 **2. Materials and methods**

### 25 2.1. Reagents and samples

1 All chemicals used were of analytical grade and used without further purification. Solutions  
2 were prepared with ultra-pure water (Millipore, resistivity > 18 MΩ cm) and stocked in high  
3 density polyethylene flasks. Lead standard solutions were prepared by dilution of a commercial  
4 1 g.L<sup>-1</sup> AAS lead stock solution (Fisher Chemical, USA) and stabilized with 1% v/v nitric acid  
5 trace metal grade (Fisher Chemical, USA). A multi-metal solution (0.037 mmol.L<sup>-1</sup> for each  
6 metal) was prepared by dissolving appropriate amounts of lead nitrate and cadmium nitrate  
7 (Alfa Aesar, USA), nickel nitrate and copper nitrate (Merck, Germany), iron (III) sulphate and  
8 potassium chromate (VI) (Prolabo, France), cobalt nitrate, zinc nitrate, and aluminium chloride  
9 (Sigma-Aldrich, USA) in ultra-pure water.

10 The commercial TrisKem Pb Resin (PB-B25-S, 50-100μm, TrisKem, France) was used for lead  
11 extraction. The elution solution was prepared from ammonium oxalate (Prolabo, France). For  
12 detection, a 0.01 mmol.L<sup>-1</sup> solution of 4-(pyridyl-2-azo)-resorcinol (PAR) monosodium salt  
13 (Merck, Germany) was prepared in a 1 mmol.L<sup>-1</sup> borate buffer solution (pH = 12).

14 Freshwater samples were collected at purposely chosen points in a coastal river “The Arc” in  
15 the south-east of France, near industrial or urban effluents discharge points. All samples were  
16 UV-photo-oxidized with a 254 nm low-pressure mercury lamp (UVP PenRay, USA) during 30  
17 minutes before analysis allowing liberation of lead linked to natural organic ligands, inorganic  
18 ligands or even to anthropogenic organic ligands.

19

## 20 2.2.Apparatus

### 21 2.2.1. Flow system

22 The three units of the MPFS system (Fig. 1) were designed with Rhinoceros® 5.0 3D software  
23 (Robert McNeel & Associates Europe, Spain), then printed with a poly(methyl methacrylate)  
24 resin on the 3D printer Form1+ (Formlabs, USA). The first unit consisted of a resin column,  
25 tightly closed by a screw piece with three entry channels for injection of sample and reagents.

1 The resin was packed in this unit between two layers of glass wool. To optimize mixing of  
2 eluate and chromogenic reagent used for lead detection (PAR), a second unit composed of a  
3 serpentine mixing coil (1.5 mm internal diameter, 50 cm length) and of a connection for PAR  
4 inlet was added to the system. Finally, the detection step was performed with a classical  
5 spectroscopic flow-cell with a 5-cm optical pathlength. Sample and reagents were introduced  
6 inside the system by means of four solenoid micro-pumps (Bio-ChemValve Inc., USA) that had  
7 a stroke volume of 20  $\mu\text{L}$  and a high frequency of 250 cycles/min. These pumps were computer-  
8 controlled by a MCFIA/MPFS system (Sciware, Spain) with eight digital 12V output channels.  
9 For the detection, two FC-UV600 optical fibres (Ocean Optics, USA) were connected at the  
10 ends of the optical pathlength, and isolated from the reaction mixture with two tailor-made  
11 quartz discs, to guide the light from the source to the spectrophotometric detector. The radiation  
12 of the halogen bulb of a DH-2000 UV-Vis light source (Ocean Optics, USA) was transmitted  
13 to a USB2000 miniature spectrometer detector (Ocean Optics, USA). The whole system was  
14 controlled by AutoAnalysis 5.0 software (Sciware, Spain).

15

#### 16 2.2.2. Metal analysis

17 Graphite furnace atomic absorption spectrometry (GF-AAS) was used to optimize the  
18 extraction/elution steps on TrisKem Pb resin and validate lead amounts in real samples (after  
19 filtration on a 0.45  $\mu\text{m}$  polyethersulfone membrane). The measurements were carried out on a  
20 Thermo Scientific ICE3500 (USA) atomic absorption spectrometer equipped with a lead  
21 hollow-cathode lamp operated at 10 mA (wavelength of 217 nm). Argon flow was 0.2  $\text{L}\cdot\text{min}^{-1}$   
22 except during atomisation step (no flow). The furnace settings were: drying at 110  $^{\circ}\text{C}$ , ramp for  
23 9 s, hold for 35 s; cracking at 800  $^{\circ}\text{C}$ , ramp for 5 s, hold for 20 s; atomising at 1200  $^{\circ}\text{C}$ , ramp  
24 for 1 s and 3 s hold; cleaning at 2500  $^{\circ}\text{C}$ , no ramp and 3 s hold.

1 Interfering cations were determined by inductively coupled plasma–atomic emission  
2 spectrometry (ICP–AES) with a Jobin YVON JY2000 Ultratrace spectrometer, equipped with  
3 a CMA spray chamber and a Meinhard R50-C1 glass nebuliser. Determinations were performed  
4 with the following settings: power 1000W, pump speed 20 mL.min<sup>-1</sup>, plasma flow rate 12  
5 L.min<sup>-1</sup>, coating gas flow rate 0.2 L.min<sup>-1</sup>, nebuliser flow rate 0.9 L.min<sup>-1</sup> and nebuliser  
6 pressure 2.08 bar.

7

### 8 2.3.Flow procedure

9 The MPFS system was operated according to the procedure in 6 steps given in Table 1: in step  
10 1, 9 mL of nitric acid solution (0.05 mol.L<sup>-1</sup>) was used for conditioning the Pb resin and washing  
11 the system before analysis. Then 50 mL of acidified sample were introduced in the system (step  
12 2). In step 3, the resin was washed again with nitric acid solution (0.05 mol.L<sup>-1</sup>) to eliminate  
13 potential interfering species extracted by the resin. 5 mL of ammonium oxalate solution (0.025  
14 mol.L<sup>-1</sup>) and PAR (0.01 mmol.L<sup>-1</sup>) were simultaneously pumped through the resin to eluate  
15 extracted lead and at the inlet of the mixing coil, respectively (steps 4-5).

16 Measurements were based on the peak height. The analytical signal was recorded at 520 nm  
17 when the elution started. Absorbance spectra were acquired every 0.5 s, with an integration  
18 time of 55 ms and an average of 3 spectra.

19

## 20 3. Results and discussion

### 21 3.1.Extraction and washing steps

#### 22 3.1.1. Influence of concentration of nitric acid

23 The developed system was based on the spectrophotometric determination of lead in the  
24 presence of PAR reagent. However, it is well known that lead determination by this simple  
25 method often suffers from interferences of cadmium, copper and zinc [25]. Therefore, the

1 concentration of these interfering metals should be reduced before PAR detection to allow  
2 selective determination of lead.

3 Lead determination was thus based on extraction properties of the resin TrisKem Pb resin. This  
4 resin was initially developed for the separation of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  and is constituted by crown-  
5 ethers diluted in isodecanol and impregnated on an inert support. The length of the carbon chain  
6 of isodecanol facilitates lead elution. Its retention capacity is 29 mg Pb/g of resin. The  
7 manufacturer's instructions recommend acidification of samples with 1 mol.L<sup>-1</sup> nitric acid  
8 before extraction of lead on TrisKem Pb resin. However, the first experiments carried out with  
9 1 mol.L<sup>-1</sup> nitric acid led, after a few injections, to yellowing and cracking of the inlet of 3D-  
10 printed column part. The effect of HNO<sub>3</sub> concentration on the extraction of lead and potentially  
11 interfering metals was thus tested in the range 0-0.1 mol.L<sup>-1</sup> in order to preserve 3D-printed  
12 parts.

13 The results in Fig. 2 showed that more than 90% of lead was extracted with HNO<sub>3</sub> concentration  
14 above 0.02 mol.L<sup>-1</sup>. The best lead extraction (97%) was obtained with HNO<sub>3</sub> 0.1 mol.L<sup>-1</sup>.

15 Concerning the other metal cations, iron was also partially extracted (20-50%, with the highest  
16 extraction at 0.1 mol.L<sup>-1</sup>). Aluminium, copper and zinc were not retained by the resin whatever  
17 the acid concentration. For HNO<sub>3</sub> concentrations of 0.02 and 0.05 mol.L<sup>-1</sup>, a very few amount  
18 ( $\leq 5\%$ ) of cobalt, chromium, and cadmium was extracted. It can therefore be concluded that the  
19 resin has an excellent selectivity for lead over other metals, except for iron for which extraction  
20 is dependent on HNO<sub>3</sub> concentration. A nitric acid concentration of 0.05 mol.L<sup>-1</sup> appeared to  
21 be sufficient to extract lead quantitatively and to limit the extraction rate of iron below 20%.

22 After metal extraction on the resin, a washing step can improve the selectivity by removing  
23 potentially interfering metals without eluting the analyte of interest. This washing step has also  
24 been studied with different HNO<sub>3</sub> concentrations. Based on the previous results, only iron and  
25 lead were studied. The washing solutions were collected and analysed by ICP-AES. As can be



1 seen in Fig. 3 the amount of both iron and lead washed out decreased with increasing HNO<sub>3</sub>  
2 concentration. With HNO<sub>3</sub> 0.02 mol.L<sup>-1</sup>, all the iron retained within the resin was eliminated,  
3 but an important lead elution rate of 42% was also observed. A nitric acid concentration of 0.05  
4 mol.L<sup>-1</sup> seems to be the best compromise between iron elimination (75%) and limited lead  
5 elution rate (about 10%).  
6 To summarize 0.05 mol.L<sup>-1</sup> HNO<sub>3</sub> may be used for both extraction and washing steps, thereby  
7 limiting the number of pumps to be used in the system.

8

### 9 3.1.2. Sample flow-rate

10 Sample flow rate was studied from 2 to 5 mL.min<sup>-1</sup> for a sample volume of 30 mL. Samples  
11 were acidified with 0.05 mol.L<sup>-1</sup> HNO<sub>3</sub> before extraction. As displayed in supplementary  
12 material (Fig. S1), results showed an important increase of lead extraction from 3 mL.min<sup>-1</sup> to  
13 5 mL.min<sup>-1</sup>. At the highest flow rate (5 mL.min<sup>-1</sup>) the extraction percentage of lead reached 94  
14 %.

15 To avoid overpressure problem of solenoid pumps or clogging of resin column, the column  
16 inner diameter and height has been set respectively at 7.8 mm and 4.5 mm, which are higher  
17 than in a traditional packed column. None of the previously mentioned problems were observed  
18 during analysis. Although solenoid pumps are not usually suitable for resin solid phase  
19 extraction, it seems that high sample flow rates enable fluidizing of the resin bed and thus good  
20 lead extraction. Therefore, a 5mL.min<sup>-1</sup> flow rate was chosen for the system.

21

### 22 3.2. Elution step

23 Ammonium oxalate is recommended by the resin manufacturer for lead elution. The lead  
24 elution has thus been studied at different concentrations of ammonium oxalate. The elution flow  
25 rate has been adjusted at 4 mL.min<sup>-1</sup>, according to the resin manufacturer instructions.

1 The results shown in Fig. 4 highlighted that elution efficiency increased with ammonium  
2 oxalate concentration up to  $0.05 \text{ mol.L}^{-1}$ .

3 For concentration of ammonium oxalate between  $0.025$  and  $0.1 \text{ mol.L}^{-1}$ , the results obtained  
4 were not significantly different. To limit reagent consumption, the concentration of ammonium  
5 oxalate was adjusted at  $0.025 \text{ mol.L}^{-1}$  for further experiments.

6

### 7 3.3. Detection

8 Lead elution profile has been studied by collecting small fractions ( $0.5 \text{ mL}$ ) of ammonium  
9 oxalate used for elution with a flow rate of  $5 \text{ mL.min}^{-1}$ . As can be seen on Fig.S2  
10 (Supplementary material), elution was complete within one minute (elution rate of 99% of total  
11 extracted lead after  $5 \text{ mL}$ ).

12 Lead was detected by spectrophotometry using a PAR solution pumped simultaneously and  
13 mixed with ammonium oxalate in the mixing coil. PAR solution was buffered with borate  
14 solution at  $\text{pH}=12$  in order to obtain a mixture at  $\text{pH}=9$  (optimised for UV-Vis detection) when  
15 mixed with ammonium oxalate which  $\text{pH}$  is around  $6.6$ .

16 PAR reagent and ammonium oxalate flow rates were studied from  $1$  to  $5 \text{ mL.min}^{-1}$ .  
17 Optimization was carried out with a standard lead solution of  $100 \mu\text{g.L}^{-1}$ . PAR flow rate was  
18 optimized using a fixed ammonium oxalate flow rate of  $5 \text{ mL.min}^{-1}$  and inversely. Fig. 5 showed  
19 that the best absorbance was obtained with the maximum flow rate of the pumps useable for  
20 the two reagents ( $5 \text{ mL.min}^{-1}$ ). The absorbance increased regularly with increasing PAR flow  
21 rate. The absorbance values increased slightly with an ammonium oxalate flow rate between  $1$   
22 and  $4 \text{ mL.min}^{-1}$  and, strongly increased for a flow rate of  $5 \text{ mL.min}^{-1}$ . This observation was  
23 consistent with results obtained for sample flow rate with better efficiency at high flow rates.  
24 However, eluent flow rate seemed to have less influence than sample flow rate. Flow rates of  
25 PAR and ammonium oxalate were thus fixed at  $5 \text{ mL.min}^{-1}$ .

1

2

### 3.4. Analytical features

3

Calibration curves have been constructed for various sample volumes (10, 25 and 50 mL). From

4

these data, limits of detection (LOD;  $3\sigma$ ;  $n=10$ ) and coefficient of variation (CV;  $n=6$ ) were

5

determined and summarized in Table S1 (Supplementary material). The analytical features

6

obtained for a 50 mL sample volume seemed adapted for typical lead concentrations in natural

7

waters: LOD was calculated at  $2.7 \mu\text{g.L}^{-1}$ , linear domain range was between 3 and  $120 \mu\text{g.L}^{-1}$ .

8

The LOD was acceptable for environmental sample analysis, but sample volume can potentially

9

be increased if lower LOD needs to be reached for water samples with very small amounts of

10

lead. An additional experiment has been carried out and a volume of 200 mL of sample has

11

been passed through the TrisKem Pb resin column. The results obtained showed that no traces

12

of lead were detected at the column outlet and that the breakthrough volume of the resin was

13

not reached. Coefficient of variation obtained with the optimal conditions (50 mL sample

14

volume), for a lead concentration of  $50 \mu\text{g.L}^{-1}$  was 5.4 %.

15

A brief comparison of previously reported flow methods for lead determination with proposed

16

3D-printed flow system is given in Table 2. Some of these methods require complicated or

17

expensive equipment in particular for detection step [26,27,29,30]. Compared to other simpler

18

flow procedures using spectrophotometric detection [28,31], the proposed method has a lower

19

detection limit better suited for analysis of natural water samples.

20

21

### 3.5. Validation

22

In order to validate the 3D-printed optimized system, five samples of freshwater have been

23

collected at purposely chosen points in a coastal river ("The Arc", south of France) in areas

24

close to anthropogenic activities. The samples were UV-photooxidized at 254 nm during 30

25

minutes and filtered at  $0.45 \mu\text{m}$  before analysis. These samples have been analyzed in duplicate

1 by ICP-AES and developed 3D-printed system with a sample volume of 50 mL, and the results  
2 were summarized in Table 3.

3 The values obtained by the two methods were consistent. The mean difference between the two  
4 methods was 5.8%, (min -11.2%; max 11.7%). The results obtained by the proposed system  
5 were compared (*t* test) with the reference method values (ICP-AES) and no significant  
6 differences at the 95% confidence level were found.

7

#### 8 **4. Conclusion**

9 A 3D-printed system was developed for determination of lead in natural waters. Lead  
10 quantification was based on the selective solid phase extraction of lead on TrisKem Pb resin  
11 followed by elution with ammonium oxalate and spectrophotometric detection using 4-(2-  
12 pyridylazo)-resorcinol as chromophoric reagent. Interferences were eliminated by optimisation  
13 of extracting and washing steps on TrisKem Pb resin. Detection limit obtained ( $2.7 \mu\text{g.L}^{-1}$ ) was  
14 consistent with environmental samples analysis but sample volume may be increased if lower  
15 detection limits are needed. The proposed flow system was compared to a reference method  
16 (ICP-AES) and was satisfactorily applied to natural waters samples. The optimized 3D-printed  
17 MPFS flow system could be controlled by an open-source microcontroller board to design a  
18 low cost portable on-line analyzer [16,17].

19

#### 20 **Acknowledgment**

21 This work was included in the project “Lab-on-Ship” funded by the French Research Agency  
22 (ANR-14-CE04-0004).

23

#### 24 **References**

25

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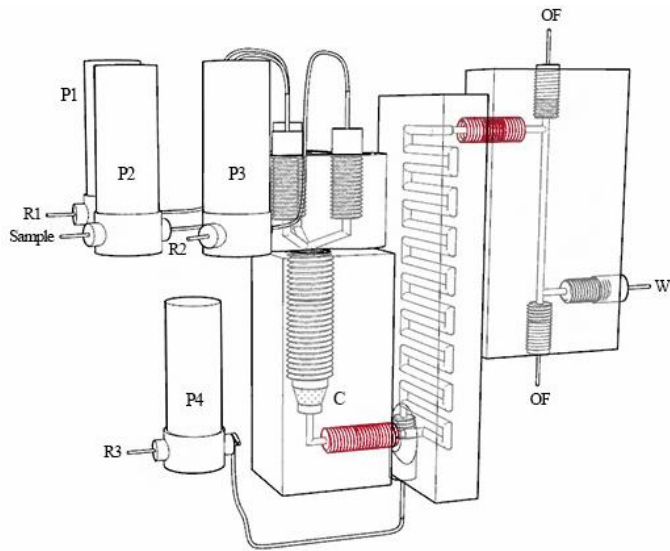
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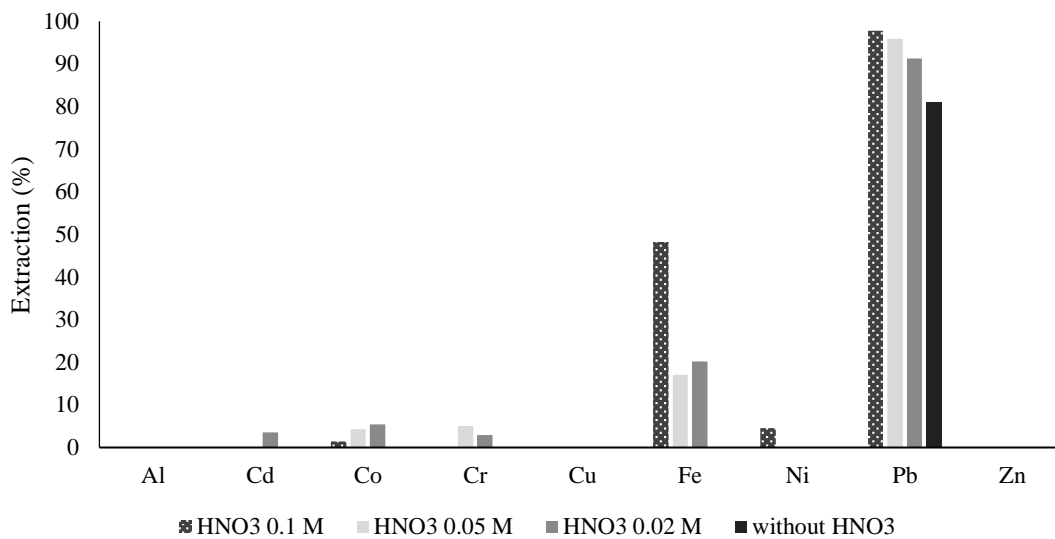




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2 **Fig. 1.** Schema of the MPFS system with the three 3D printed units. C: resin column, R1: nitric  
 3 acid, R2: ammonium oxalate, R3: PAR, OF: optical fiber, W: waste. In red, the screws and  
 4 corresponding screw threads to assemble the units.

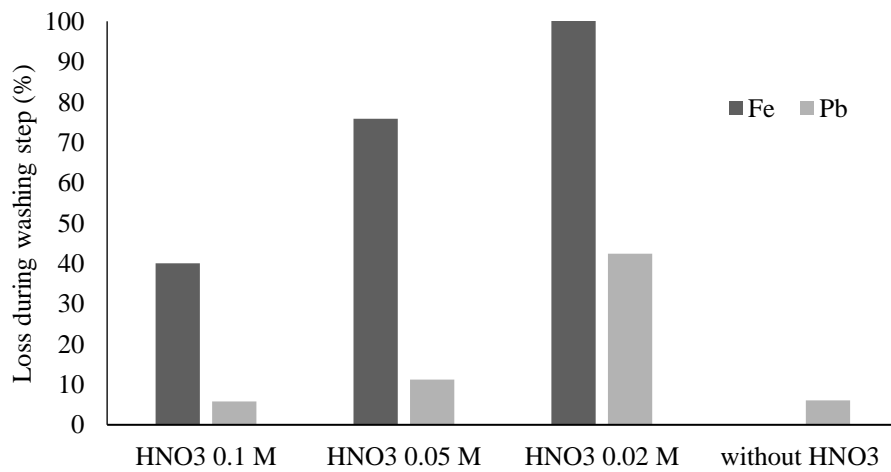
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2 **Fig. 2.** Extraction of several metals on TrisKem Pb resin for different concentrations of nitric  
 3 acid [multi-metal solution at  $0.037 \text{ mmol.L}^{-1}$  ( $V = 30 \text{ mL}$  at  $3 \text{ mL.min}^{-1}$ ), nitric acid at  $5 \text{ mL.min}^{-1}$   
 4 ( $V = 9 \text{ mL}$  for conditioning step,  $V = 6 \text{ mL}$  for washing step), ammonium oxalate at  $0.1 \text{ mol.L}^{-1}$   
 5 ( $V = 10 \text{ mL}$  at  $4 \text{ mL.min}^{-1}$ ).

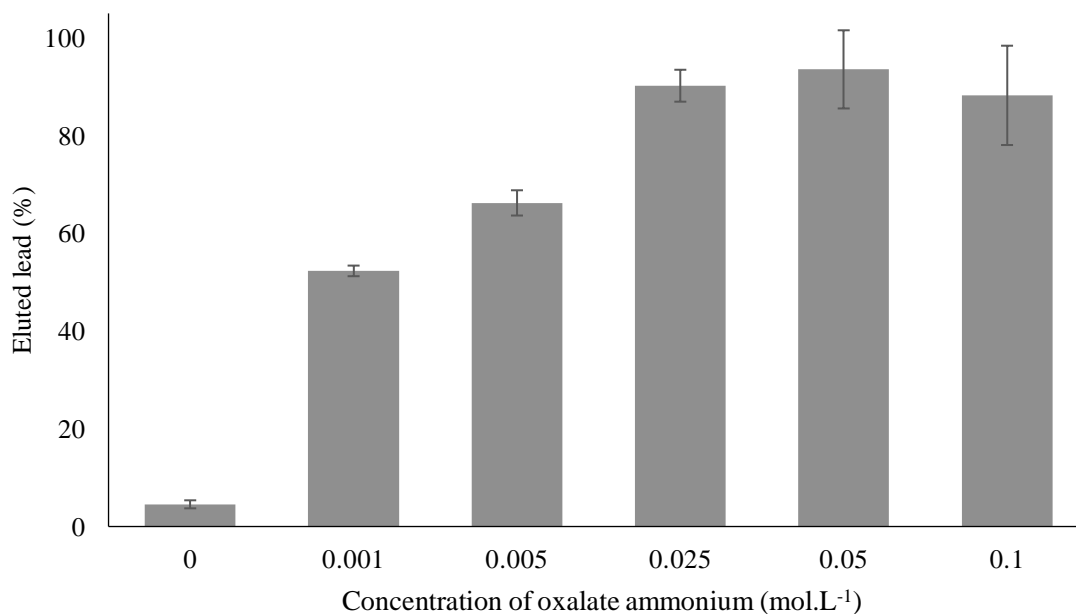
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1

2 **Fig. 3.** Iron and lead washing out during washing step [multi-metal solution at  $0.037 \text{ mmol.L}^{-1}$   
 3 ( $V = 30 \text{ mL}$  at  $3 \text{ mL.min}^{-1}$ ), nitric acid at  $5 \text{ mL.min}^{-1}$  ( $V = 9 \text{ mL}$  for conditioning step,  $V = 6$   
 4  $\text{mL}$  for washing step), ammonium oxalate at  $0.1 \text{ mol.L}^{-1}$  ( $V = 10 \text{ mL}$  at  $4 \text{ mL.min}^{-1}$ ).

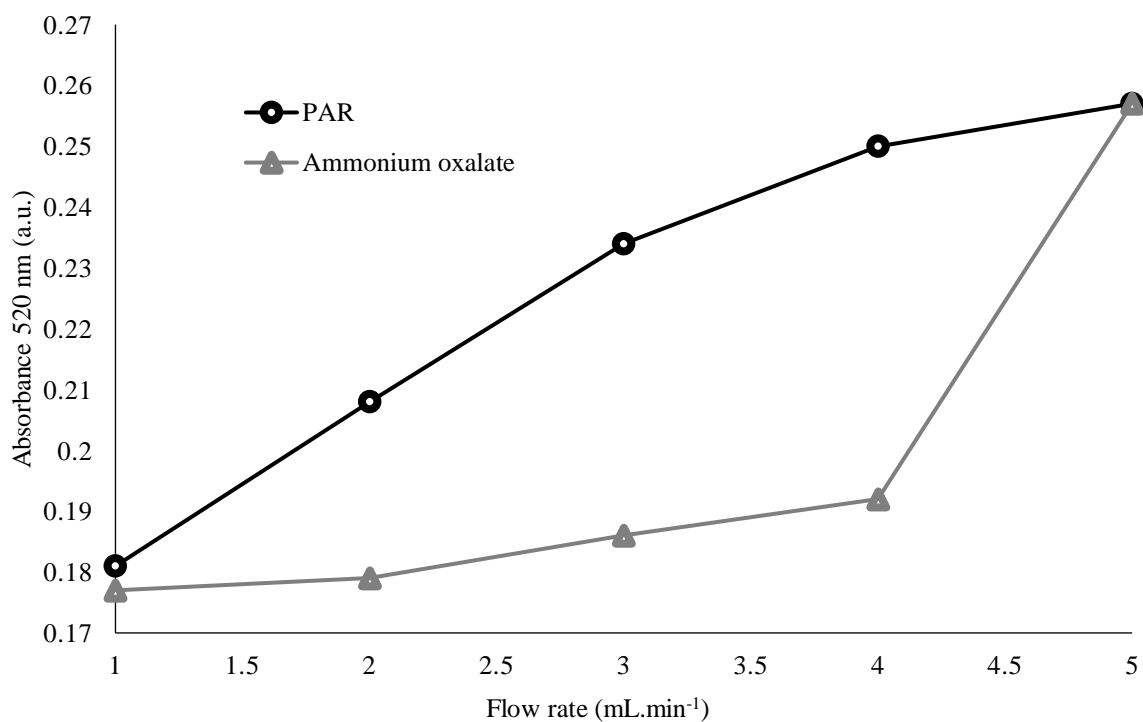
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2 **Fig. 4.** Elution of lead at different concentrations of ammonium oxalate [lead solution at 100  
3  $\mu\text{g.L}^{-1}$  ( $V = 30 \text{ mL}$  at  $5 \text{ mL.min}^{-1}$ ), nitric acid at  $0.05 \text{ mol.L}^{-1}$  ( $V = 9 \text{ mL}$  for conditioning step,  
4  $V = 6 \text{ mL}$  for washing step, at  $5 \text{ mL.min}^{-1}$ ), ammonium oxalate at  $4 \text{ mL.min}^{-1}$  ( $V = 10 \text{ mL}$ )].

5



1

2 **Fig. 5.** Absorbance versus PAR and ammonium oxalate flow rates [lead solution at  $100 \mu\text{g.L}^{-1}$   
 3 ( $V = 30 \text{ mL}$  at  $5 \text{ mL.min}^{-1}$ ), nitric acid at  $0.05 \text{ mol.L}^{-1}$  ( $V = 9 \text{ mL}$  for conditioning step,  $V = 6$   
 4  $\text{mL}$  for washing step, at  $5 \text{ mL.min}^{-1}$ ), ammonium oxalate at  $0.025 \text{ mol.L}^{-1}$  ( $V = 10 \text{ mL}$ ), PAR  
 5 at  $0.01 \text{ mmol.L}^{-1}$  ( $V = 10 \text{ mL}$ )].

6

1 **Table 1** Flow procedure for lead determination in water

<b>Step</b>	<b>Description</b>	<b>Action</b>	<b>Volume (mL)</b>	<b>Flow-rate (mL.min<sup>-1</sup>)</b>	<b>P1</b>	<b>P2</b>	<b>P3</b>	<b>P4</b>
1	Conditioning	Pumping nitric acid	9	5	ON	OFF	OFF	OFF
2	Pb extraction	Pumping sample	50	5	OFF	ON	OFF	OFF
3	Washing	Pumping nitric acid	6	5	ON	OFF	OFF	OFF
4	Start data acquisition	-	-	-				
5	Elution & detection	Pumping ammonium oxalate and PAR	5	4	OFF	OFF	ON	ON
6	Stop data acquisition	-	-	-				

2

3

1 **Table 2** Comparison of flow methods for lead determination in water samples.

2

Reference	Flow technique <sup>a</sup>	Preconcentration mode <sup>b</sup>	Detection system <sup>c</sup>	Linear range ( $\mu\text{g}\cdot\text{L}^{-1}$ )	Precision (%)	LOD ( $\mu\text{g}\cdot\text{L}^{-1}$ )
[26]	SI-LAV	LPME	FAAS	6 – 300	2.9	1.8
[27]	LOV	SPE	HG-AFS	0.014 – 20	2.4	0.004
[28]	FIA	SPE	Vis	25 – 250	4.5	5
[29]	SI	DLLME	FAAS	2.3 – 160	1.9	0.54
[30]	SI-LOV	BI	ETAAS	2 – 8	1.9	0.6
[31]	SI	SPE	Vis	50 – 300	4	25
Present work	MPFS	SPE	Vis	3 – 120	5.4	2.7

3

4 <sup>a</sup> MPFS: multipumping flow system; SI-LAV: sequential injection – lab-at-valve; LOV: lab-  
 5 on-valve; FIA: flow injection analysis; SI : sequential injection; SI-LOV: sequential injection  
 6 – lab-on-valve

7 <sup>b</sup> LPME : liquid phase micro-extraction ; SPE : solid phase extraction ; DLLME: dispersive  
 8 liquid-liquid micro-extraction; BI: bead injection

9 <sup>c</sup> FAAS: flame atomic absorption spectrometry; Vis: visible spectrophotometry; HG-AFS:  
 10 hydride generation-atomic fluorescence spectroscopy; ETAAS: electrothermal atomic  
 11 absorption spectrometry

12

13

1 **Table 3** Lead determination in real natural water samples with optimised 3D-printed flow  
2 system vs reference method (ICP-AES).

Samples	Lead concentration ( $\mu\text{g/L}$ )	
	ICP-AES	3D system
Industrial zone (electronic manufacturing) (upstream)	$17.4 \pm 1.6$	$15.8 \pm 2.5$
Industrial zone (electronic manufacturing) (downstream)	$15.1 \pm 0.8$	$13.8 \pm 1.5$
WWTP (upstream)	$16.5 \pm 1.8$	$18.7 \pm 2.1$
WWTP (direct downstream)	$17.4 \pm 2.2$	$16.6 \pm 0.8$
River – (12km downstream)	$12.9 \pm 0.4$	$11.6 \pm 1.4$

3

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