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Exploration of alternative routes for recycling critical metals from waste PCB and tantalum capacitors

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ABSTRACT

Printed Circuit Boards (PCB), secondary source of critical metals, are usually recycled to recover precious metals. Alternative routes, aiming to pre-concentrate critical metals, were tested at lab scale. An up-scaling process is proposed involving a thermomechanical separation of PCB and surface mounted devices (SMD). PCB without SMD are treated by solvolysis for desilication and debromination. Further calcination provides a presumably leachable metallic mix. Tantalum capacitors, a specific type of SMD, are treated by pyrolysis, to isolate metallic cores, which are further leached to obtain 92% pure tantalum oxide. LCA data show that tantalum recycling process is profitable for the environment.

1. Introduction

The development of new technological equipment may be hindered by a predictable lack of crucial resources. During the last two decades, some chemical elements of confidential applications, became key elements for the miniaturization of IT equipment. Many of these critical elements are dispersed in materials, and as the market for IT equipment only increases, the supply of such resources tends to come at risk (Alves Dia et al., 2018).

Urban Mining can mitigate this risk, by recycling elements present in Waste Electrical and Electronic Equipment (WEEE), such as Printed Circuit Board (PCB). A PCB is a multilayer of epoxy resin, copper foils and glass fibers (Meng et al., 2018), containing all the electric connections between integrated circuits and other surface mounted devices (SMD). SMD contain most of the critical materials in the WEEE (Gonda et al., 2018). *Nomenclature*

KOH	Sodium hydroxide
PCB	Printed Circuit Board
SMD	Surface Mounted Devices
WEEE	Waste electrical and electronic equipment
XRF	X-Rays Fluorescence spectroscopy

Landfilling and incineration are prohibited for PCB bigger than 10 cm² (Directive 2012/19/EU), due to PCB pollutants: heavy metal and brominated flame retardants (degrading above 800 °C) (Ni et al., 2012; Moosakazemi et al., 2019).

The actual recycling process generally consists in a smelting at high temperature with separation in lead and copper liquid phases (Wan et al., 2018), to recover precious metals (gold, silver and platinum group), which are more present in waste PCB than in their respective ores (Wansi et al., 2018). Smelting has a non-negligible impact on the environment (Ghodrat et al., 2017). Other techniques as hydrometallurgy (Moosakazemi et al., 2019) and biometallurgy (Ning et al., 2017) require further advanced treatment (Meng et al., 2018; Meng et al., 2019).

Depending on the refining treatment, side metals may be recovered, but these techniques mainly focus on the recovery of copper and lead. Most critical materials, such as tantalum, are dispersed in slags (Nassar, 2017).

Tantalum is a critical metal whose main application is the production of capacitors. Tantalum capacitors are yellow or black colored SMD composed of a center of metallic tantalum and dielectric tantalum oxide, surrounded by layers of manganese oxide, carbon and silver (Chen et al., 2018). That central block is surrounded by a thick epoxy layer, containing silica powder. This limits the recycling of tantalum capacitors, because silica and tantalum oxides have a similar chemical reactivity (Wansi et al., 2018). Consequently, less than 1% of end of life tantalum is nowadays recycled (Ueberschaar et al., 2017). Routes involving ionic liquids extraction (Micheau et al., 2019; Chen et al., 2019) or N,N-dioctyl-

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1-octanamine extraction (Spitczok von Brisinski et al., 2014) are in development, but require hazardous reactants. Techniques to separate the tantalum core from resin are in development with steam gasification (Katano et al., 2014), supercritical water (Niu et al., 2017), vacuum pyrolysis (Chen et al., 2018) and neutral atmosphere pyrolysis (Niu et al., 2017). These techniques are promising but still remain pre-concentration techniques and need further tantalum purification.

The present study explores alternative routes to pre-concentrate critical elements. It compares two different methods to degrade epoxy resin and avoid the emission of brominated fumes: thermal decomposition (calcination and pyrolysis) and solvolysis. The influence of the waste composition is also studied; three types of samples were treated: non treated PCB, PCB from which were removed the SMD and tantalum capacitors as a model of SMD. An attempt of leaching on tantalum capacitors residues was led to obtain purified tantalum. The environmental impact of tantalum recycling is evaluated through LCA (life cycle assessment) data.

2. Experimental procedures

2.1. Materials

The two PCB samples originate from end-of-life data servers; one has been cut into pieces of ~5 × 5 cm without further treatment. This PCB supports tantalum capacitors and other SMD. This sample is further termed “PCB with SMD”.

The other PCB has been heated for a few minutes at 100 °C in order to soften the tin solder joints, then all SMD have been detached with a hot scraper. The PCB has then been cut into pieces. This sample is further termed “PCB without SMD”.

The tantalum capacitors originate from PCB from end-of-life data servers. They have been removed from the PCB with tweezers under local heating by an infrared lamp and a hot air nozzle, allowing the solder joints to melt.

2.2. Characterizations

The elemental composition of the samples, before and after treatment, has been obtained by wavelength dispersive X-Rays fluorescence spectroscopy (XRF, *S4Pioneer, Bruker*), after excluding imprecise measurements of carbon and nitrogen.

2.3. Calcination and pyrolysis experiments

Firstly, the samples have been thermally characterized by simultaneous thermal analysis (*STA 409PC, Netzsch*) from 0 to 1000 °C under both oxidative (air flow) and neutral atmosphere (helium flow), in order to assign the correct temperature for the calcination and the pyrolysis experiments, respectively.

Alumina crucibles containing approximately 5 g of sample have been inserted into a tubular furnace under air flow or N_2 flow (120 L/h). They were heated up to 700 °C at a rate of 600 °C/h, maintained at 700 °C for 30 min and then cooled down naturally. Exhaust gases have been flushed in two consecutive bubblers, one containing sodium hydroxide solution and one containing water, to trap halogenated gas.

2.4. Solvolysis

Solvolysis reactors (*DAB-2, Berghof*), containing each approximately 1g of PCB without SMD, 10 mL of solvent: pure water, a mix of water and methanol (1:3, 1:1, 3:1) or methanol, and 5g of potassium hydroxide (KOH), have been heated up to 250 °C at a rate of 125 °C/h, maintained at 250 °C for 12 h and allowed to cool down naturally. The maximum allowed pressure is 200bars. Reactors have also been prepared with pure water, mix water-methanol (1:1) and methanol without KOH. Samples of all types were reacted with pure water, and methanol with KOH.

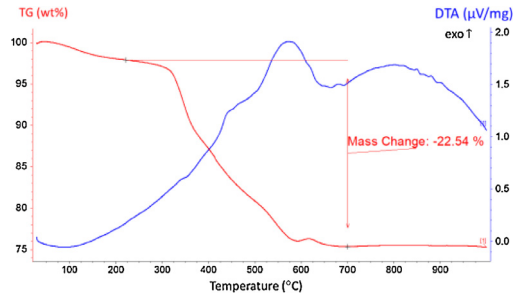

Fig. 1. Thermogram of a PCB without SMD under air flow: showing mass change in thermogravimetric analysis (TG) in red and heat exchange in differential thermal analysis (DTA) in blue.

2.5. Tantalum purification

Six tantalum capacitors have been thermally decomposed under N_2 flow. The remaining solid has been sieved, to separate the epoxy residues and the metallic cores. After crushing, the latter have been immersed for four hours in nitric acid (20mL per gram of powder) at room temperature, then filtered and dried.

3. Results and discussion

3.1. Composition of the samples

The major chemical elements detected in PCB without SMD are copper, oxygen, silicon and bromine (Table 1). Minor fractions are magnesium (6.2%), lead (3%) tin (2.7%) and calcium (1.8%). Common side elements are found at fractions lower than 1%: sulfur, chlorine, sodium, iron, potassium. Strontium, titanium and chromium can be found at fraction lower than 0,1%.

For PCB with SMD, the global composition is similar (Table 2). Barium is highly present in this sample, probably as barium titanate, in dielectric ceramic capacitors. Silver, aluminum, gold, gallium, nickel, phosphorus and tantalum are also found in small proportions.

No precious nor critical metal can be detected in PCB without SMD, but some can be detected in PCB with SMD at fractions lower than 1%. Critical and precious metals, gathered in SMD, are present at low concentrations.

Capacitors are mainly composed of tantalum (Table 3). They contain bromine (0.5%) and antimony (1.3%), both used in flame retardants. They also contain aluminum, iron, nickel, titanium and zinc at fractions lower than 1%.

3.2. Thermal characterization

This orientation test shows that a two-step degradation occurs under oxidative atmosphere, degrading approximately a quarter of the mass of the sample. Fig. 1 shows first a drying of the sample at ~100 °C, then organic matter calcination implying H_2O and CO losses, at ~350 °C and CO_2 released between 500 and 650 °C.

Under neutral atmosphere, the degradation, presumably a pyrolysis, occurs below 700 °C as well. Thus, to ensure that the degradation processes take place during the thermal degradation treatment, the furnace temperature has been set at 700°C.

Table 1
Elemental composition (weight percentage of elements) of PCB without SMD: before any treatment, after thermal degradation (air flow and N_2 flow) and after solvolysis, in presence of water and in presence of methanol and sodium hydroxide.

Chemical element (wt%)	Before treatment	Thermal decomposition		Solvolysis	
		N_2 flow	Air flow	Water	Methanol + KOH
Cu	23	50	35	33	25
O	21	7	27	23	26
Si	20	23	15	19	25
Br	19	0.2	0.2	20	1,0
K	0	0.1	0.1	0	5.5
Other	17	20	22	5	18

Table 2
Elemental composition (weight percentage of elements) of PCB with SMD: before any treatment, after thermal degradation (air flow and N_2 flow) and after solvolysis, in presence of water and in presence of methanol and sodium hydroxide.

Chemical element (wt%)	Before treatment	Thermal decomposition		Solvolysis	
		N_2 flow	Air flow	Water	Methanol + KOH
Cu	25	43	29	22	12
O	20	8	28	28	27
Si	10	20	19	10	0
Br	9	0	0	9	4
Ba	17	3	1	16	2
K	0	0	0	0	52
Other	20	25	22	14	2

Table 3
Elemental composition (weight percentage of elements) of crushed tantalum capacitors; before any treatment, after pyrolysis (metallic core), after calcination and after solvolysis, in presence of water and in presence of methanol and sodium hydroxide.

Chemical element (wt%)	Before treatment	Thermal decomposition		Solvolysis	
		N_2 flow	Air flow	Water	Methanol + KOH
Ta	6	73	23	20	20
Si	35	0	29	25	24
O	45	18	38	43	38
Ag	0.2	0,0	0.6	0.7	0.7
Mn	2	8	5	7	9
Br	0,4	0.2	0.5	0.8	0.9
K	0	0	0	0	1.5
Other	10	1	3	3	5

3.3. Thermal degradation

The thermal degradation was conducted either as pyrolysis (with N_2 flow) and calcination (air flow) for each sample. The visual aspect of the samples before and after treatment (Fig. 2), highlights contrasted behaviors. PCB, treated in oxidizing conditions, are almost fully degraded as gaseous carbon oxides and residues keep their original color. In neutral atmosphere, the resin transforms into a dark carbon deposit. Actually, the oxygen fraction in all samples is lower after pyrolysis than after calcination (Tables 1–3).

For PCB with SMD, there is a second reason for the dark coloring: the tin, present in solder joints, melts below 232 °C, and solidifies in dark patches when the sample cools down. Those patches of molten tin are present after calcination and pyrolysis. Due to this melting, SMD are separated from PCB during thermal treatment.

For both pyrolysis and calcination, molten tin glues the remaining layers together. A proper separation of the multi-layers (woven glass fibers, copper foils and carbon residues in the case of pyrolysis) would require a mechanical intervention. Since the layers are thin and friable, any mechanical treatment would turn them into a complex mix of powders, limiting the possibility of preconcentration.

For tantalum capacitors, the calcination oxidizes the tantalum core and makes it friable. As a crushing is needed to separate the core from epoxy residues, the core is transformed into tantalum oxide powder. Thus, it cannot be sieved from silica powder contained in degraded epoxy shell (Table 3), hindering a leaching as they have a similar reactivity. With pyrolysis, the metallic core remains solid and can be sieved from silica powder and crushed epoxy residues. The metallic core, recovered this way contains up to 73% of tantalum.

The proportion of bromine is reduced during the treatment. This implies the emission brominated gases. They are trapped by bubblers at the experimental scale, but in case of up-scaling, the treatment of the fumes must be carefully considered. A primary debromination treatment can be an adequate scenario, this is the scope of the following section.

3.4. Solvolysis

Eight solvents have been tested in sub-critical conditions, aiming to develop a method combining debromination and desilication, hoping to recover the whole quantity of metals. Due to the quantity of results, the presented results (Tables 1–3 and Fig. 2) are restricted to the most representative conditions. The evolution of bromine and silicon in all conditions is also presented in Fig. 3.

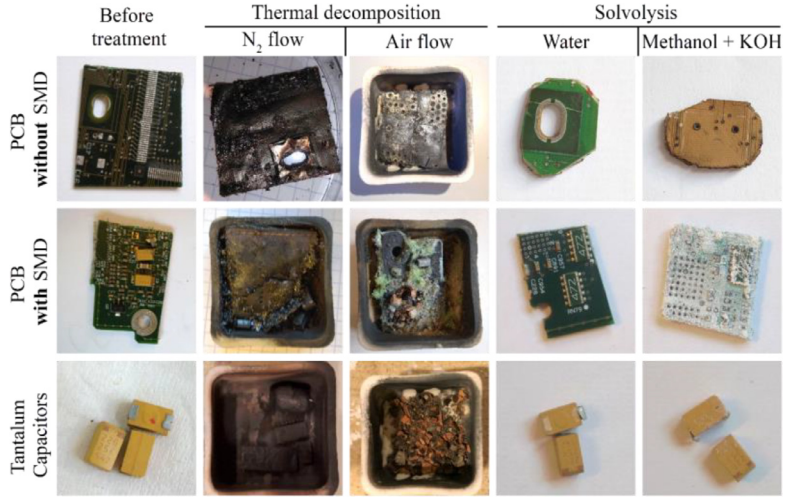

Fig. 2. Photograph of the samples (PCB without SMD, PCB with SMD and tantalum capacitors) before treatment, after thermal decomposition under N_2 flow and air flow, and after solvolysis in presence of water and in presence of methanol and sodium hydroxide.

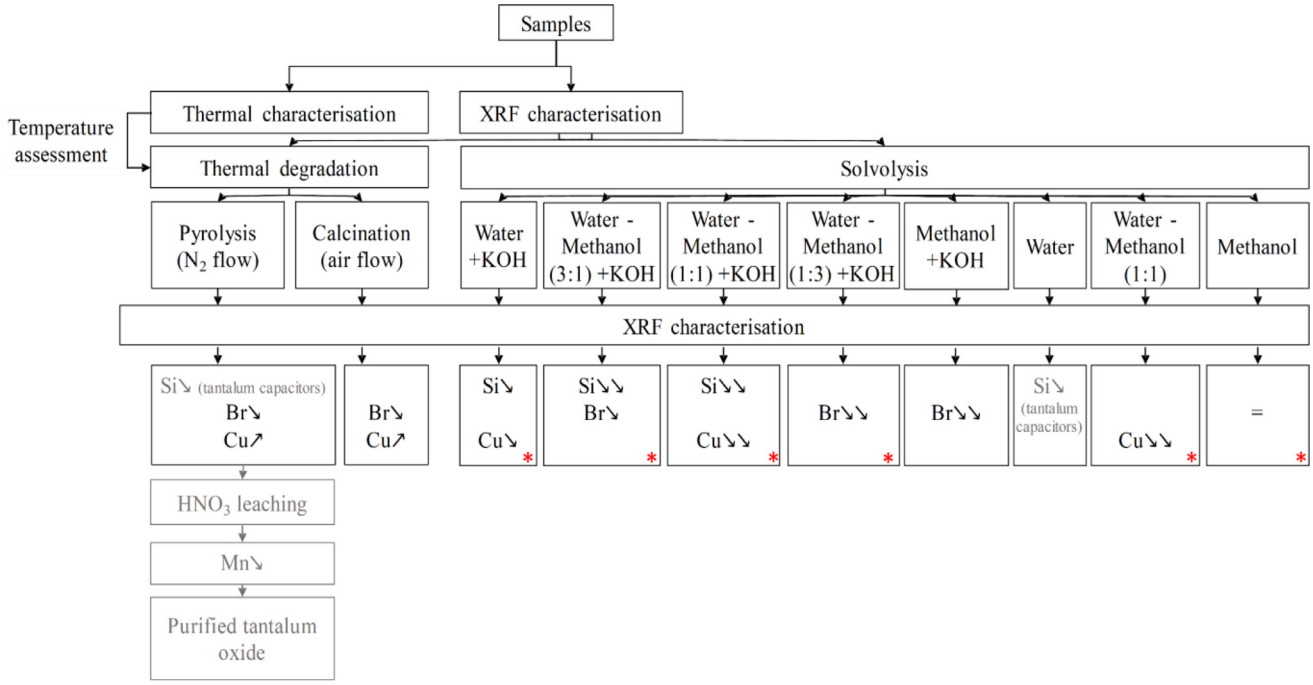

Fig. 3. Experimental plan of the present study and the main impact on the chemical composition, with leaching of tantalum capacitors in grey and conditions tested only on PCB without SMD marked by a red asterisk.

Actually, solvolysis operated without KOH, does not have the desired impact as it does not affect either the bromine or silicon content in the samples, except for silicon oxide in tantalum capacitors treated in pure water. Moreover, an unwanted dissolution of copper is observed for mixed water and methanol (1:1). This holds true for the same solvent mix in presence of KOH.

A dissolution of silicon oxide, up to 75%, is observed in the more polar conditions (water, water-methanol 3:1 and water-methanol 1:1 in presence of KOH). This is probably due to an interaction between silica and hydroxide to form soluble metasilicates. The reaction might be the same for capacitors in pure water, favored by the small size of the silica particles compared to woven glass fibers. For tantalum capacitors, for which silica isolation would be particularly interesting, the solubilized fraction is lower than for PCB, probably due to the thickness of the epoxy resin.

Debromination is only observed in the combined presence of methanol and KOH, and particularly efficient in the case of mixed water-methanol (1:3) in presence of KOH (up to 91%) or methanol in presence of KOH (up to 95%).

Thus a complete debromination and desilication cannot be achieve in a single step, but the treatment with water-methanol (3:1) in presence of KOH seems a good compromise as it allows a desilication up to 72% and a debromination up to 30%.

For further studies, a key parameter is the quantity of potassium hydroxide: crystallized KOH covers the samples, as can be seen on Fig. 2 (methanol+KOH, PCB with SMD) and is confirmed by the proportion of potassium observed by XRF. This suggests an

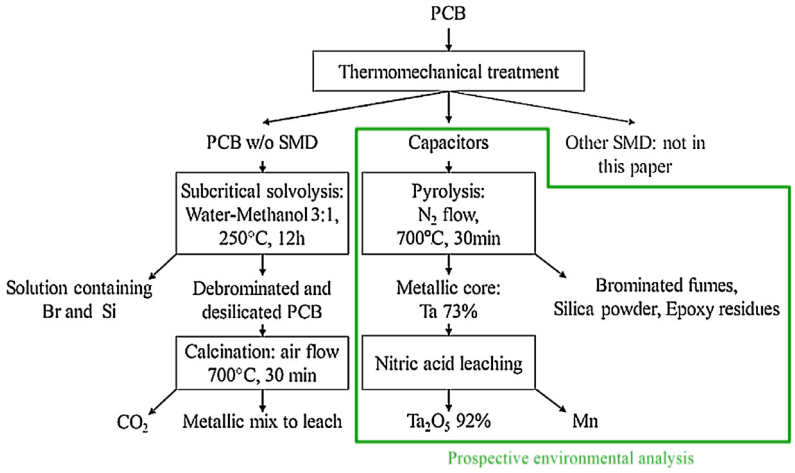

Fig. 4. Proposed routes for up-scaling: PCB without SMD treatment and tantalum capacitors.

Table 4
Elemental composition of tantalum metallic cores of capacitors before and after purification with nitric acid.

Chemical composition (wt%)	Before leaching	After leaching
Ta_2O_5	88	92
MnO	10	6
Al2O3	1.3	1.4
Fe2O3	0.2	0.1
Br	0.2	0.1

Table 5
Most relevant inputs (+) and outputs (−) of tantalum recovery process, per kg of capacitors.

Product	Quantity
N_2, liquid	+ 50 kg
HNO_3	+ 2.512 kg
Acid purification (proxy: H_3PO_4 purif.)	+ 2.512 kg
Process heat (measured at lab scale)	+ 6.873 MJ
Avoided bromine emission (to air)	−3.6 g
Ta_2O_5	−155,6 g

excess of KOH and that the same efficiency can be reached with reduced quantities of KOH.

3.5. Purification of tantalum residues

As can be seen in Table 4, the nitric acid leaching efficiently purifies the tantalum extracted from capacitors after pyrolysis, as it reduces the proportion of manganese oxide. As the tantalum is present as tantalum pentoxide (confirmed by XRD measurements) because of the highly oxidizing condition of the leaching, tantalum pentoxide represents 92% of the mass of the remaining powder after one leaching. Considering a process involving cascade leaching, one can even improve that purity.

3.6. Prospective environmental analysis

From the lab scale, LCA data can be generated. It is assumed that the Ta is extracted following the second branch of Fig. 4 and recycled as Ta_2O_5 powder. The PCB without SMD are sent to the classical smelting process and are out of the perimeter of the analysis: the Br removal process (left branch Fig. 4) is excluded, due to a lack of data. The analysis compares the avoided damages due to the Ta recovery, with the already identified burdens that are a consequence of its recovery, the other elements being treated following the current industrial practice. The functional unit is 1 kg raw capacitors treated and the selected life cycle impact assessment method is ReCiPe (endpoint, hierarchist). The calculation is performed using SimaPro v 8.4.0.0 Multi-user with Ecoinvent 3 database. The inputs and outputs are summarized in Table 5. The nitrogen amount is based on non-optimised lab scale results. The same stands for HNO_3 that might be recycled for the same use, reducing the net amount needed per kg of capacitors. The process heat used for the pyrolysis should be compensated by the energy recovery from the pyrolysis products (char), but this benefit was not measured. Finally, Br might be extracted from the process,

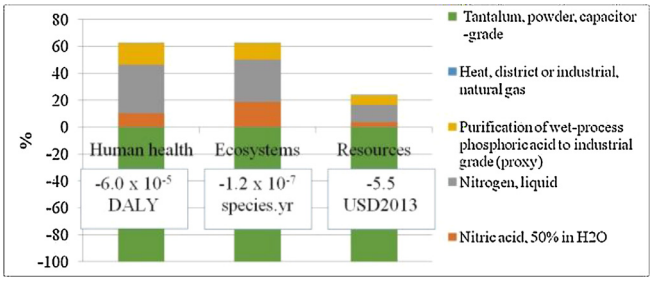

Fig. 5. LCIA data of the avoided production of Ta powder (<0) and the needed commodities (>0).

avoiding direct emissions from the classical smelting process, but the associated damage is not measured in ReCiPe.

Fig. 5 compares the avoided damage of the Ta powder production and of the above mentioned commodities. For the three endpoint categories, the damages are lower than the environmental benefits. The analysis may be refined by including the infrastructure, the thermomechanical separation process and the complete description of internal recycling and exhaust gas treatment. However, the use of consumables in excess in this experimental study (conservative assumption) is an encouragement for further studies on the recovery of Ta.

4. Conclusion

Based on the results, an up-scaling is suggested in Fig. 4. Pyrolysis followed by nitric acid leaching is proposed for the extraction of tantalum from capacitors. For PCB, solvolysis is proposed as debromination and desilication treatment, followed by a calcination of the organic fraction.

Here, solvolysis is a pre-treatment because it does not fully degrade epoxy resin. It only allows a desilication up to 72% and de-

bromination up to 30% with water-methanol (3:1) in presence of KOH.

Pyrolysis is selected for the tantalum recovery. The metallic cores are recovered after crushing and sieving, in contrast to calcination which generates a complex mix of powder. Acid leaching leads to tantalum oxide with 92% purity. LCA data suggests that this treatment is environmentally advantageous, even for those non optimized conditions, as it avoids the high impacting Ta powder production.

Its implementation requires common equipment and reactants contrary to hydrometallurgy gasification, supercritical water solvolysis. However, no soft condition could be identified for recycling. It requires several steps inevitably involving at least intermediate temperature treatment and strong basic/acid reagents.

CRediT authorship contribution statement

Frédérique Bastin: Investigation, Formal analysis, Methodology, Validation, Resources, Visualization, Writing - original draft, Writing - review & editing. **Aurélien Janssen:** Investigation, Formal analysis, Methodology. **Yannick Lolivier:** Investigation, Formal analysis, Methodology. **Murilo Masalskas:** Investigation, Formal analysis, Methodology. **Adrien Van Rechem:** Investigation, Formal analysis, Methodology. **Pierre D'Ans:** Conceptualization, Supervision, Writing - original draft, Writing - review & editing.

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