INNOVATIVE HYDROMETALLURGICAL TREATMENTS OF WEEE

SOS.TE.N.ERE

ITIA-CNR
29/01/2018

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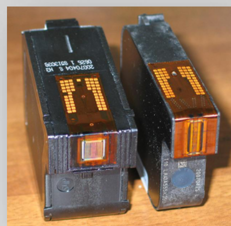
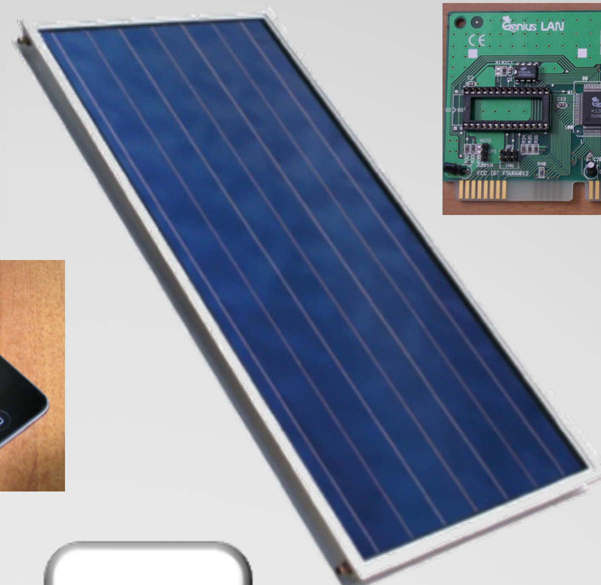
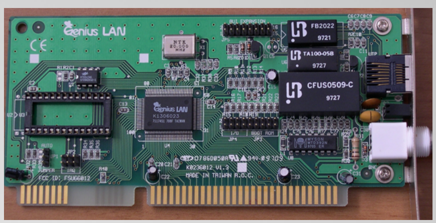
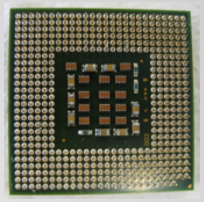
- NM are crucial components of several **E**lectric and **E**lectronic **E**quipments (**EEE**)

Au Pd Cu Ag Ir Rh Pt

Noble-Metals (NM) based technologies

Estimed depletion of raw materials

- NM reserves will be deplated in few years

Estimed depletion of known reserves at the current rate of extraction*

Au

5-50 years

Pt

Rh

Ag

Ir

Pd

50-100 years

Cu

- Most of them are listed as critical metals by EU**

**RSC Green Chemistry Element Recovery and Sustainability, N. 22, 2013, Chapter 1, Hunt*

***Report of the Ad-hoc Working Group on defining critical raw materials, 30 July 2010 and May 2014.*

- **No longer working**
- **no longer interesting**
- **no longer performing**

… Hi-Tech goods!

- Fast technological development → Reduces lifespan & increases demand for Hi-Tech goods
- Planned obsolescence

High rate of element consumption & WEEE accumulation

2014

41.8M t/year worldwide
(5% all municipal waste)

9.1M t/year in **EU**

3-5% growth/year

Waste EEE (WEEE)

The worldwide fastest growing waste stream!

General scope: preserving the environment and natural sources; limiting or avoiding hazardous substances

Objective: limiting WEEE to be disposed of, by promoting recovery.

EU waste management priorities:

- **prevention or reduction of waste**
- **recovery of waste**
- **waste as a source of energy**

improved by:

- product design to limit hazardous substances and favour material recovery.
- safe processes for waste recovery or disposal.

European Directives:

91/156/EC on waste management

2012/19/EU on WEEE

2011/65/EU on restriction of the use of certain hazardous substances in EEE (RoHS)

"polluter pays" **and "producer responsibility" principles**

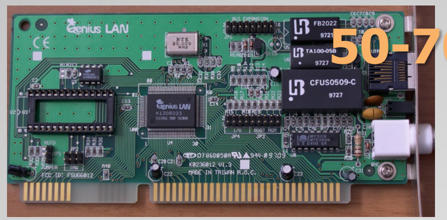
Collection rate: 85% of generated WEEE (~20Kg/year *per capita*)

EU Directives on Waste Management

Gold in WEEE *vs* MINES

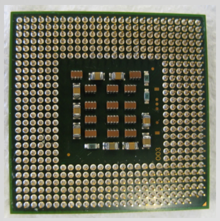
"Urban mine"

- PBCs



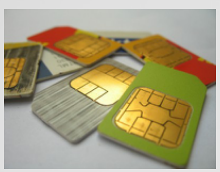
50-700g/t

- CPUs



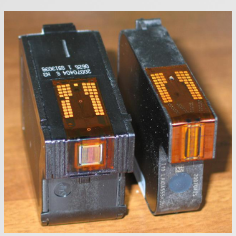
4Kg/t

- Sim and smart cards



1Kg/t

- Printer cartridges



100g/t

Gold mine

Costs for metal extraction:
385 $/oz (15 euro/g)

Gold mine in Sardinia:
2-4 g/t Au

WEEE are valuable secondary source of NMs

- **"Volatile" quotation and high price (euro/g, 28/01/'18):**

  Au 35; Rh 44; Pt 26; Pd 28; Ag 0.45

- **Recovery rates of NMs from wastes still too low**

  ~ **30% Au; 12% Ag; 27% Pd; 22% Pt**, in 2015

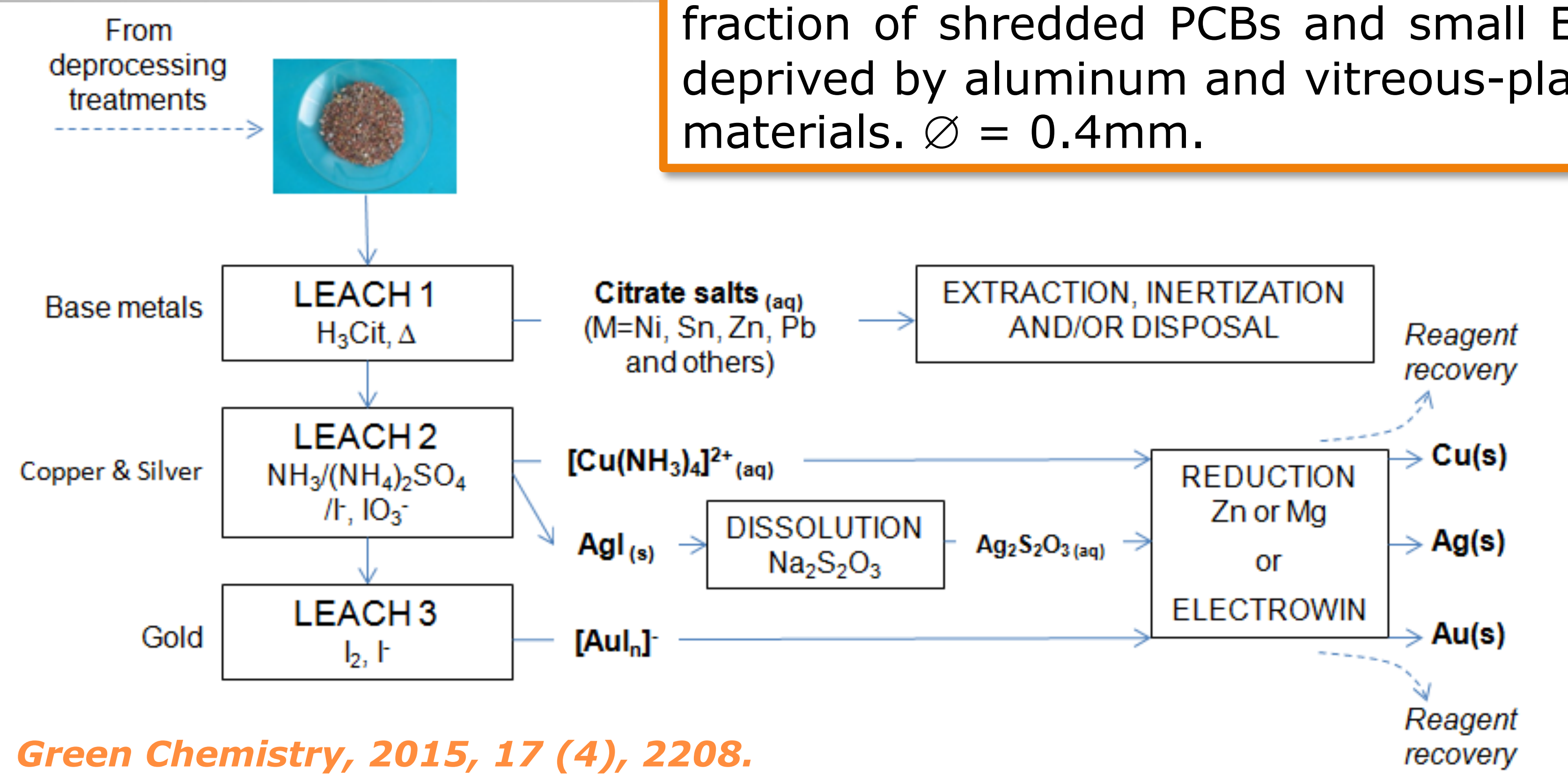
- **NMs recovery from WEEE mainly performed by using hazardous and/or polluting processes "inherited" by ore reclamation**

NEED OF

Robust, versatile and "green" processes to achieve economical-technical-environmental sustainability for NMs recovery in a Circular Economy model.

From "trash" to "resource"

Test specimen: non-ferrous metallic fraction of shredded PCBs and small EEE, deprived by aluminum and vitreous-plastic materials. ∅ = 0.4mm.



Green Chemistry, 2015, 17 (4), 2208.

- NM recovery occurs in an almost quantitative yield
- Reagents can be recycled
- Safe reagents and mild reaction conditions

Sustainable NM recovery method for WEEE

Jointly by companies:

Activity		Phase
Selection of PBCs as target WEEE	Abundant and NM-rich waste stream	
Characterization of the different typologies of existing PCBs	Lack of a robust and detailed database	**1**
Selection of the target PCB	In terms of NM content and sample availability	
Collection and shredding of the test specimen	Low cost milling treatment	**2**
NM Leaching & recovery process	Effect of grain size and interfering materials	
Scale-up on pilot plant	#R #G #M	**3**

Technology transfer

- Selection and pre-treatments

Typology	n.	Starting weight [g]	Weight after shredding: First stage [g]	Weight after shredding: Second stage [g]	Weight loss %	Elements removed before shredding
DVD/CD players PCBs	7	220,0	220,0	214,8	2,1	Motors and rotating supports (334 g)
NICs[a]	13	642,6	639,6	635,1	1,2	Fasteners (14,4 g)
RAM[b] white fingers	50	703,3		702,6	0,1	
RAM[b] gold fingers	40	676,5		667,1	1,4	
Hard drive PCBs	5	98,3	98,0	95,5	2,9	Heads and motors (768.3 g)
Mother boards[c]	5	2525,4	2510,8	2486,7	1,5	
TV PCBs	5	1985,3		1947,4	1,9	Ferrous parts (142,3 g)
Mobile phone PCBs	30	695,7		694,1	0,2	

[a]Network Integrated Controllers; [b]Random Access Memories; [c]Shredded with connectors

1st stage: single shaft shredder comminution (output: ∅ = 10mm).

2nd stage: cutting mill (1500 rpm; meshed grid: 2 mm, hardmetal tools).

Internal cleaning of the machine was performed after each treatment, in order to avoid contamination and loss of precious materials.

Phase 1: Characterization of PCBs

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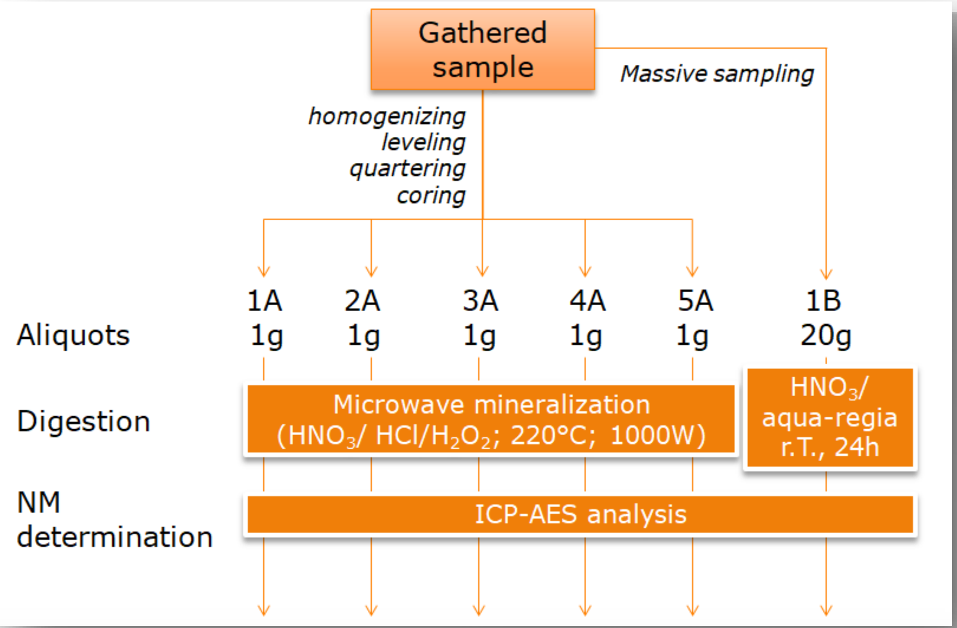
- Sampling
- Digestion
- ICP-AES analysis



Sample	NMs content - %(SD)			
	Pd	Au	Ag	Cu
DVD/CD players PCBs	<0.01*	0.01(±0.01)	0.08(±0.05)	16.2(±4.4)
NICs	<0.01*	0.02(±0.01)	0.03(±0.01)	19.1(±2.3)
RAM white fingers	0.04(±0.03)	0.03(±0.01)	0.10(±0.06)	16.6(±1.9)
RAM gold fingers	0.01(±0.01)	0.07(±0.01)	0.05(±0.01)	17.1(±1.2)
Hard drive PCBs	0.02(±0.02)	0.03(±0.01)	0.06(±0.05)	23.6(±4.9)
Mother boards	<0.01*	0.01(±0.01)	0.04(±0.02)	26.7(±5.4)
TV PCBs	<0.01*	<0.01*	0.03 (±0.01)	13.0(±7.4)
Mobile phone PCBs	0.06(±0.02)	0.07 (±0.01)	0.14 (±0.25)	33.8(±1.1)

*The concentration of this element is lower than the Limit of Detection of the measure.

Phase 2: Test specimen

- Shredding

Mix RAMs 200g

Ball milling →

- 24h, r.T.
- stainless steel jar planetary apparatus: 4-stages mill, 300rpm
- hardmetal balls: Ø 6 mm, 1.4Kg
- Carbsyn: 250mL

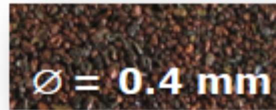
- Characterization

Wide particle size dispersion:
106g Ø <2mm
94g Ø>2mm
Presence of composite vitreous-plastic material

Element	*RAM #R#G#M* Content %(SD)
Au	0.08 (±0.03)
Ag	0.04 (±0.01)
Pd	0.06 (±0.04)
Cu	15 (±1)
Ni	4.2 (±0.7)
Fe	7 (±3)
Cr	<0.01
Mn	0.06 (±0.02)
Pb	0.8 (±0.5)

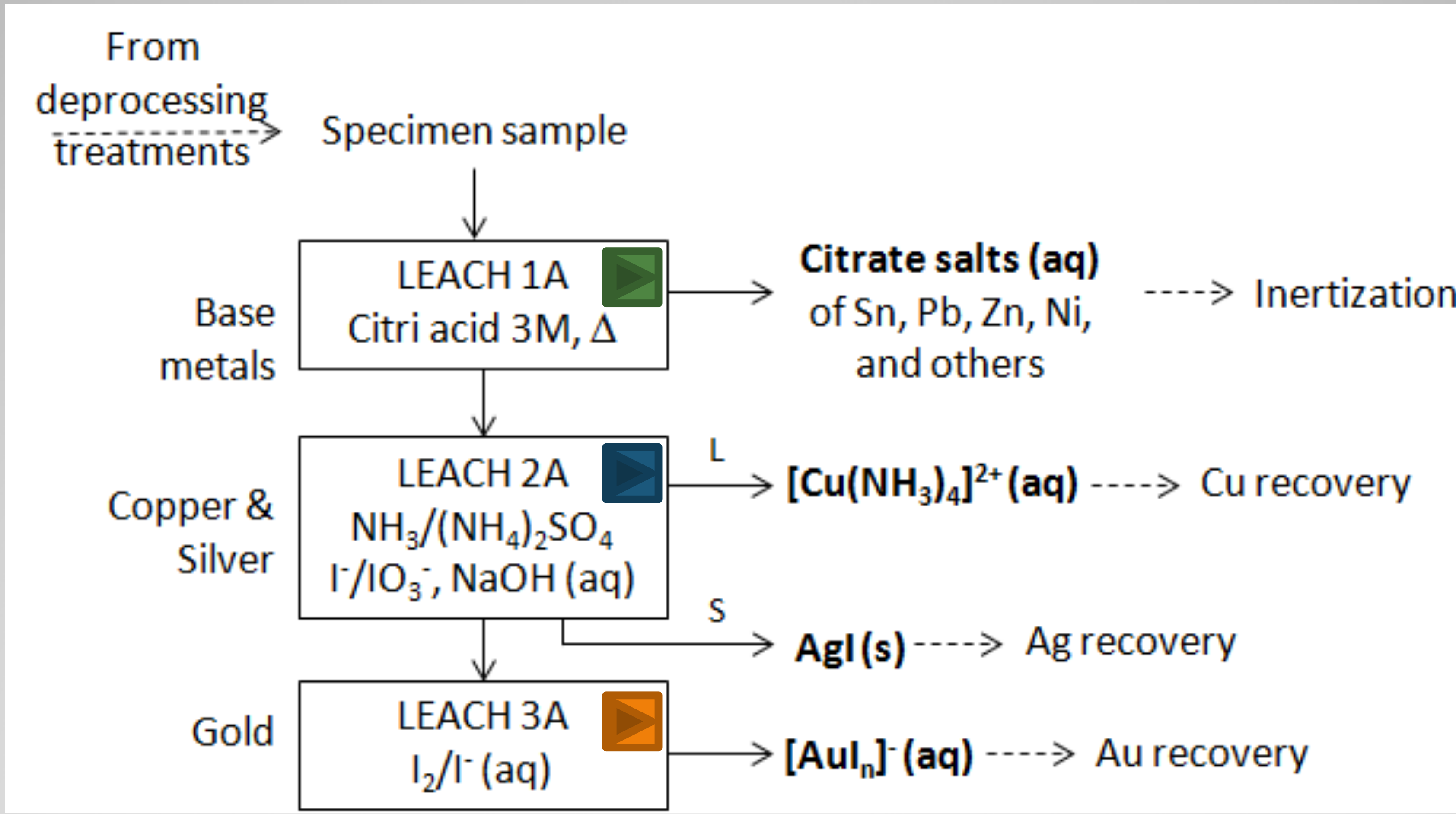
- ICP-AES analysis on N. 3 aliquotes (1.5g each) digested under microwaves
- High SD→heterogeneous material

Reference *vs* selected sample

Me	RAM #R#G#M	Reference sample
		
	% w/w	% w/w
Au	0.08	0.01
Cu	15	79
Ag	0.04	0.06
Ni	4	0.5
Fe	7	1
Cr	0.07	
Mn	0.06	
Pb	0.8	7
Sn	n. a.	10

- **RAM #R#G#M**
  - Coarse material
  - Metallic fraction ~ 30% of the sample
  - Presence of ferrous materials
  - Presence of vitreous-platic material
  - Low cost pre-treatments

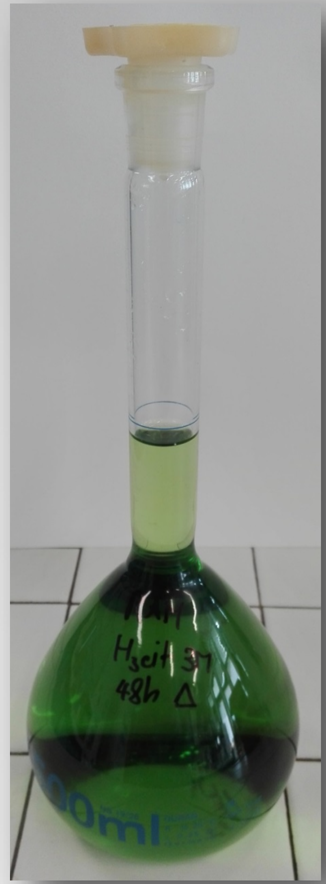
- **Reference sample**
  - Thin powder material
  - Deprived by non-metallic materials
  - Deprived by ferrous materials
  - More costly treatments and equipments



Phase 2: leaching & recovery

- Base metal dissolution

Leach conditions		Base metals %	Leach. time (ref.)	Leach. time (obs.)	Dissolution Yield
Citric Acid 3M, Δ	A	~20	48h	48h	Almost quantitative
	B	~20	48h	48h	Almost quantitative (+25% Cu)



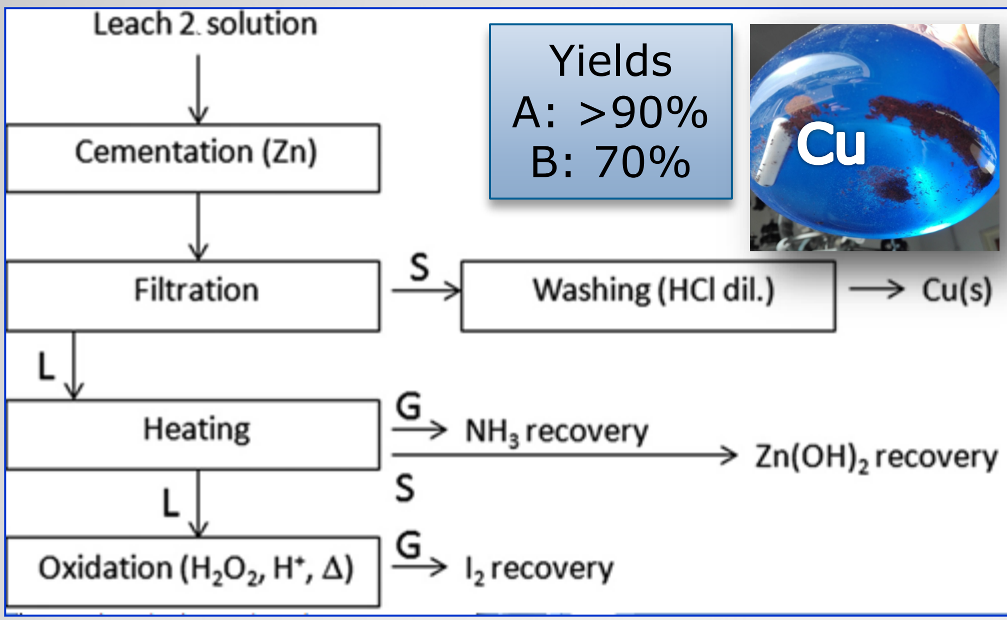
Sample A: Reference
Sample B: RAM #R#G#M

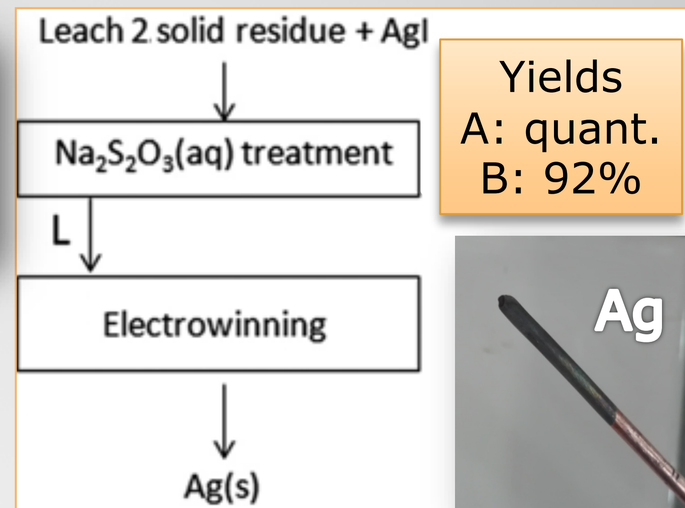
Selecivity can be improved by tuning the leaching time and working under inert atmosphere (N_2)

Phase 2: Leach 1

- Copper and silver dissolution and recovery

Leach conditions		Metals %	Leach. time (ref)	Leach. time (obs.)	Leaching products
$NH_3/(NH_4)_2SO_4$ I^-/IO_3^- (OH^-)	A	Cu ~80 Ag 0.06	48h	48h	$[Cu(NH_3)_4]^{2+}$(aq) AgI(s)
	B	Cu ~15 Ag 0.04	9h	96h	



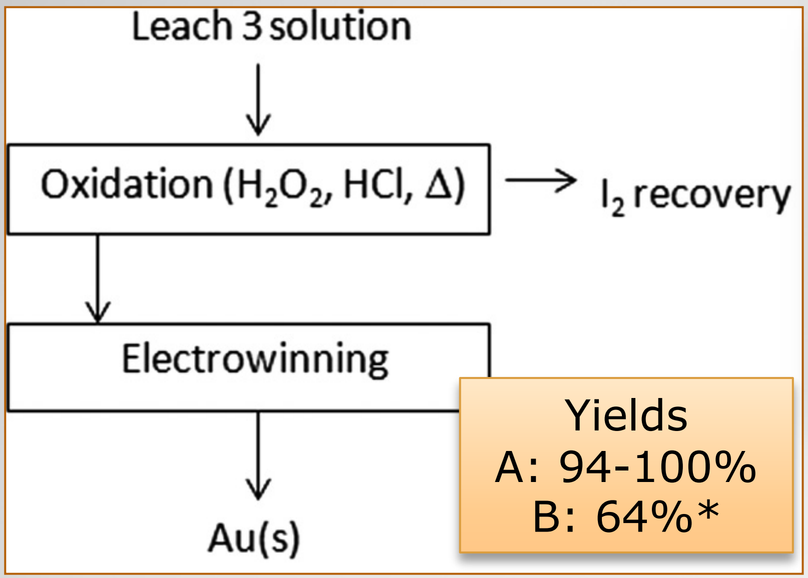


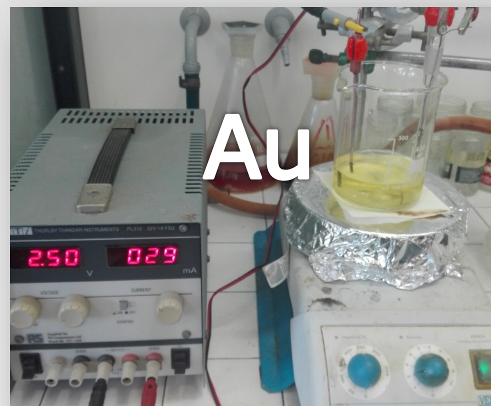
Phase 2: Leach 2

Phase 2: Leach 3

- Gold dissolution and recovery

Leach conditions		Au %	Leach. time (ref)	Leach. time (obs.)	Leaching products
I^-/I_2 (aq) 5:1	A	0.01	30′	30′	$[AuI_4]^-$(aq)
	B	0.08	30′	30′	





*The solid residue contains the missing 36% of Au, 5% of Cu and a small amount of Ag.

Conclusions: leaching process

- As expected, the effectiveness of the process is higher towards the sample A than B, thanks to its greater surface area and limited presence of interfering species.

- Nevertheless, the coarseness of the material does not seem jeopardize the process:
  - Leach 2 (Cu) was the most affected requiring leaching times 10-times longer than expected → gradual exposure of copper hidden by the vitreous-plastic support matrix.
  - A slight further effort in combining the pre-treatment set up with the subsequent leaching processes would help in obtaining the optimal conditions to meet the effectiveness and sustainability required for practical application.

Conclusions and perspectives

- Systematic characterization of the NM content in different typologies of PCB by quantitative chemical analysis.
- On the basis on the PCBs characterization and the described preliminary results, a scale-up of the process on a pilot scale **(Phase 3)** will be performed thanks to the #Recovery #Green #Metal project supported by companies through the crowdfunding platform WithYouWeDo TIM

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Co-founders #Recovery #Green #Metal

TIM, Roma
Gold fixing, Padova
Valori e Preziosi, Padova
Oro Market, Mestre (VE)
Ri.Tech, Matera
OMCD, Anzola d'Ossola (VB)
Ecocopper, Carasco (GE)
CO.RE.M., Sestu (CA)

CO.RE.M. Srl

RI.TECH Srl

Acknowledgements

Industrial methods for NM recovery

Two main alternative approaches "inherited" by ore reclamation:

1. **Pyrometallurgical treatments**

- Efficient
- High costs (energy intensive)
- High environmental impact (e.g. gas emissions)
- Unselective

2. **Hydrometallurgical methods**

Conventional

Cyanidation in alkaline media

Strong oxidising acids (e.g. aqua regia)

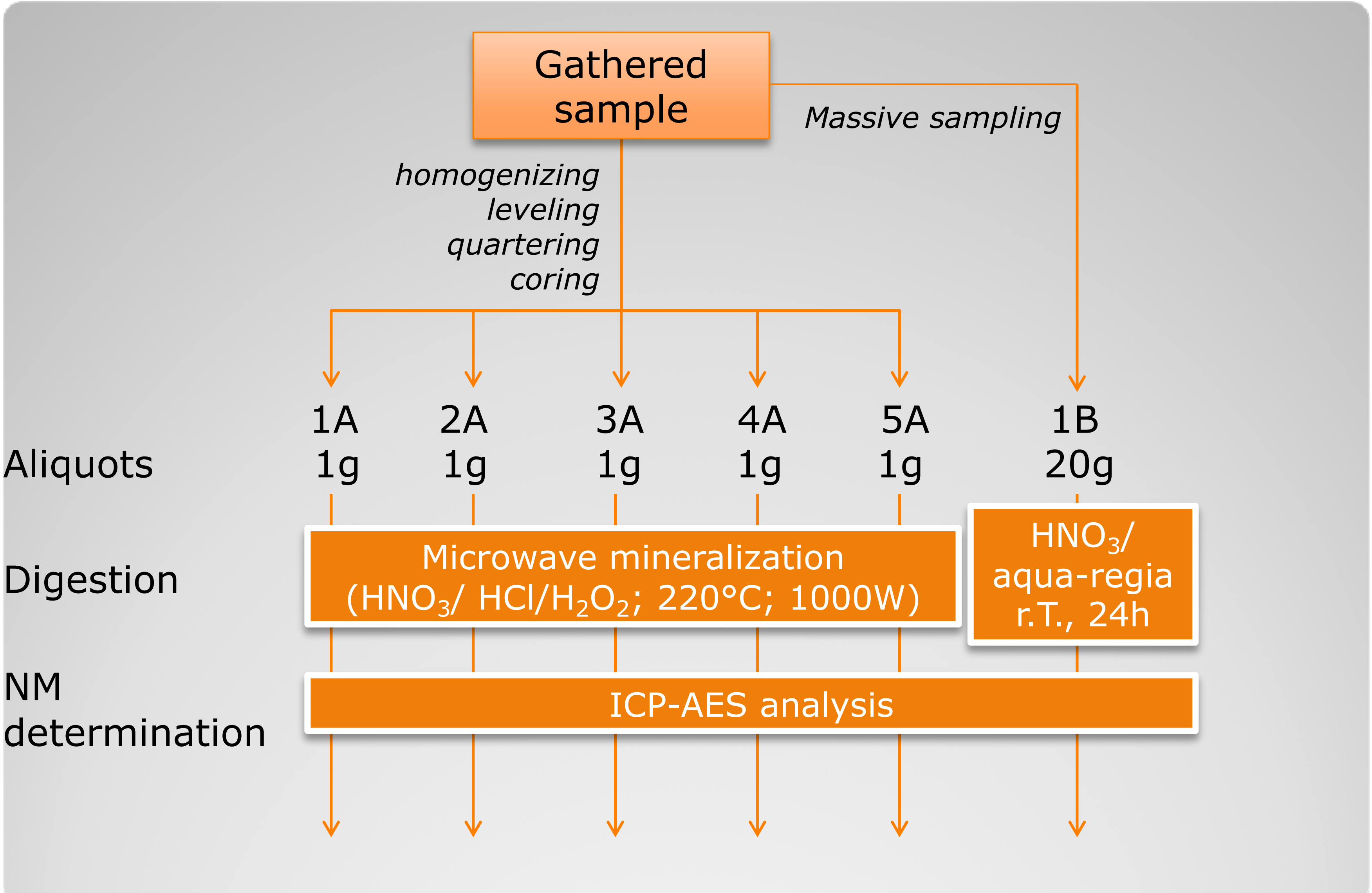
- Relatively selective
- Effective
- Low cost
- Dangerous reagents
- Gas emissions
- Wastewater

Alternative

Thiosulfate or Thiourea in oxidising environment (O_2, Fe^{3+},…)

- Relatively selective
- Effective
- Low cost
- Safer reagents
- High reagent consumption

- Sampling, digestion, ICP-AES analysis



CHARACTERIZATION OF PCBs