Joint Workshop of Junior Research - JWJR

Environmental, social and economic sustainability

EVALUATION OF AN ENVIRONMENTAL FRIENDLY METHOD FOR THE POLYMERIC E-WASTE DIGESTION FOR FURTHER Br AND METALS DETERMINATION

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ELECTRICAL AND ELECTRONIC EQUIPMENT

EEE

Essential to our modern way of life

- **Mobile phone, computer, TV, among others.**

- **Improved performance and reduced cost in each new generation of product**
- **Encourage unsustainable behaviour**
- **Mobile phones: often treated as fashion items replaced long before their design lifetimes have expired**

Electronic Waste (E-Waste)

ELECTRONIC WASTE

- Discharge
- Recycling

Waste management is difficult:

- Hazardous components
- Formation of hazardous substances

Legislation to overcome the increase in generated e-waste

➢ **Brazil: there is no specific policy for this type of material**

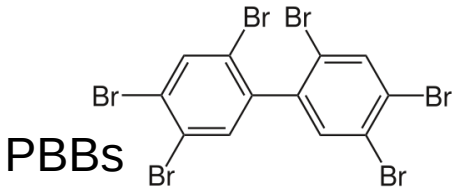
- CONAMA: disposal of batteries
- National Policy on Solid Waste Management: producer responsibility

Hester, R. E., Harrison, R. M., Electronic waste management, The Royal Society of Chemistry, 2009
Ongondo, F. O. *et al*, *Waste Manage.* 31 (2011) 714-730

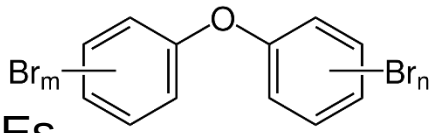
ELECTRONIC WASTE

Composition

- Printed circuits boards
- Polymers or blends
- Additives (chemical, thermic and mechanical resistance)
- Brominated compounds (polybrominated biphenyls - PBBs- and polybrominated diphenylethers -PBDEs-)



PBBs



PBDEs

➢ **Additives: contain toxic elements, as Sb, Cd, Hg**

↳ **Toxic to the environment and human lives**

Legislation: Europe

- **Directive 2011/65/EU (Restriction of the Use of Certain Hazardous Substances, RoHS)**
  - Cd (0.01%)
  - Cr(VI), Hg, and Pb (0.1%)
  - Polybrominated compounds (0.1%)
    - → PBB and PBDE

- **Sb: not specified in the Directive**
  - → Used as flame retardant

- **Polybrominated compounds: about 50% (m/m) of Br**
  - → Bromine determination (indirect determination of compounds)

Hester, R. E., Harrison, R. M., Electronic waste management, The Royal Society of Chemistry, 2009
Ongondo, F. O. *et al.*, *Waste Manage.* 31 (2011) 714-730

BROMINE AND METALS DETERMINATION IN POLYMERS

SAMPLE IN SOLUTION → **SAMPLE PREPARATION STEP**

- HIGH STABILITY
- RESISTANCE TO ACID ATTACK
- DIGESTS MUST BE SUITABLE FOR THE DETERMINATION TECHNIQUES

→ Use of concentrated acids

BROMINE AND METALS DETERMINATION IN POLYMERS

SAMPLE IN SOLUTION

SAMPLE PREPARATION STEP

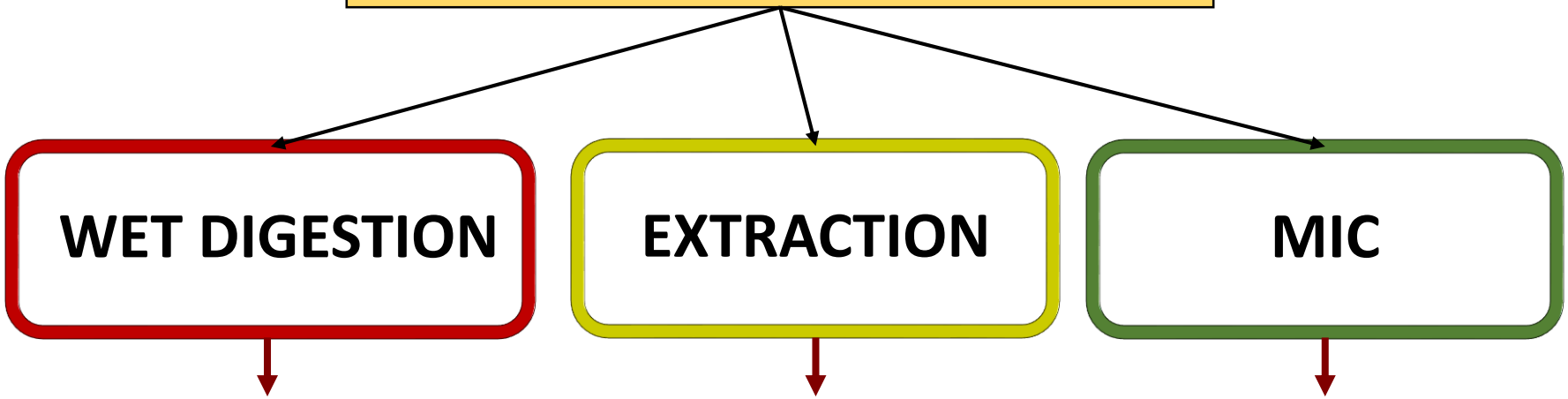
Analytical Challenge

- **HIGH STABILITY**
- **RESISTANCE TO ACID ATTACK**
- **DIGESTS MUST BE SUITABLE FOR THE DETERMINATION TECHNIQUES**

→ **Use of concentrated acids**

Flores, E. M. M., Microwave-assisted sample preparation for trace element determination, Elsevier, 2014, pp. 99-142.

Sample preparation step

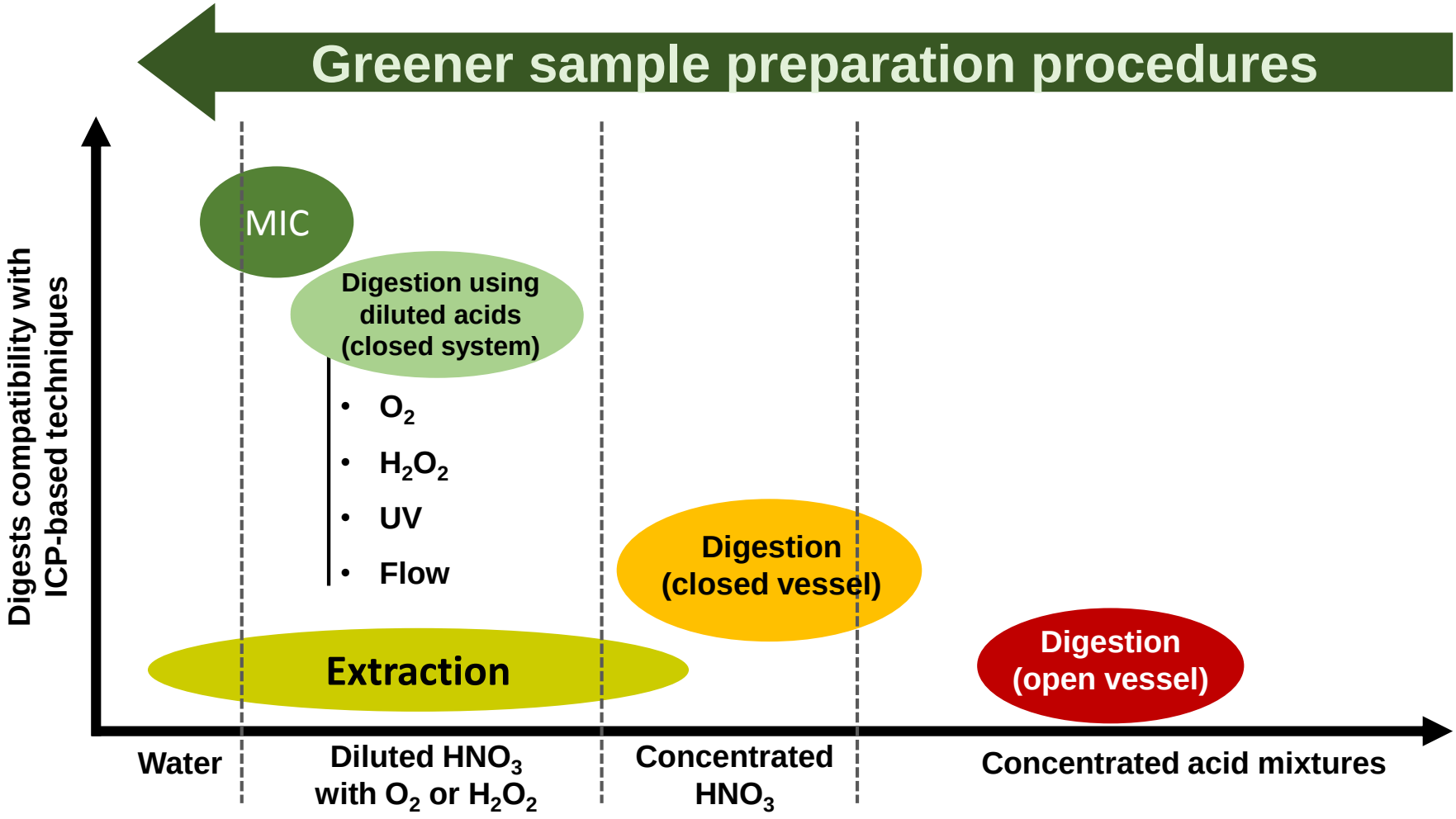


WET DIGESTION	EXTRACTION	MIC
✓ Fast heating of the solution	✓ High sample mass	✓ Low carbon content
✓ High temperature	✓ High temperarute	✓ Diluted solutions
× Concentrated acids	× Reproductibility	× Cost
× High carbon content	× Extraction efficiency	
× High residual acidity	× High carbon content	

Problem: there is no single protocol for bromine and metals

MIC: Microwave-Induced Combustion

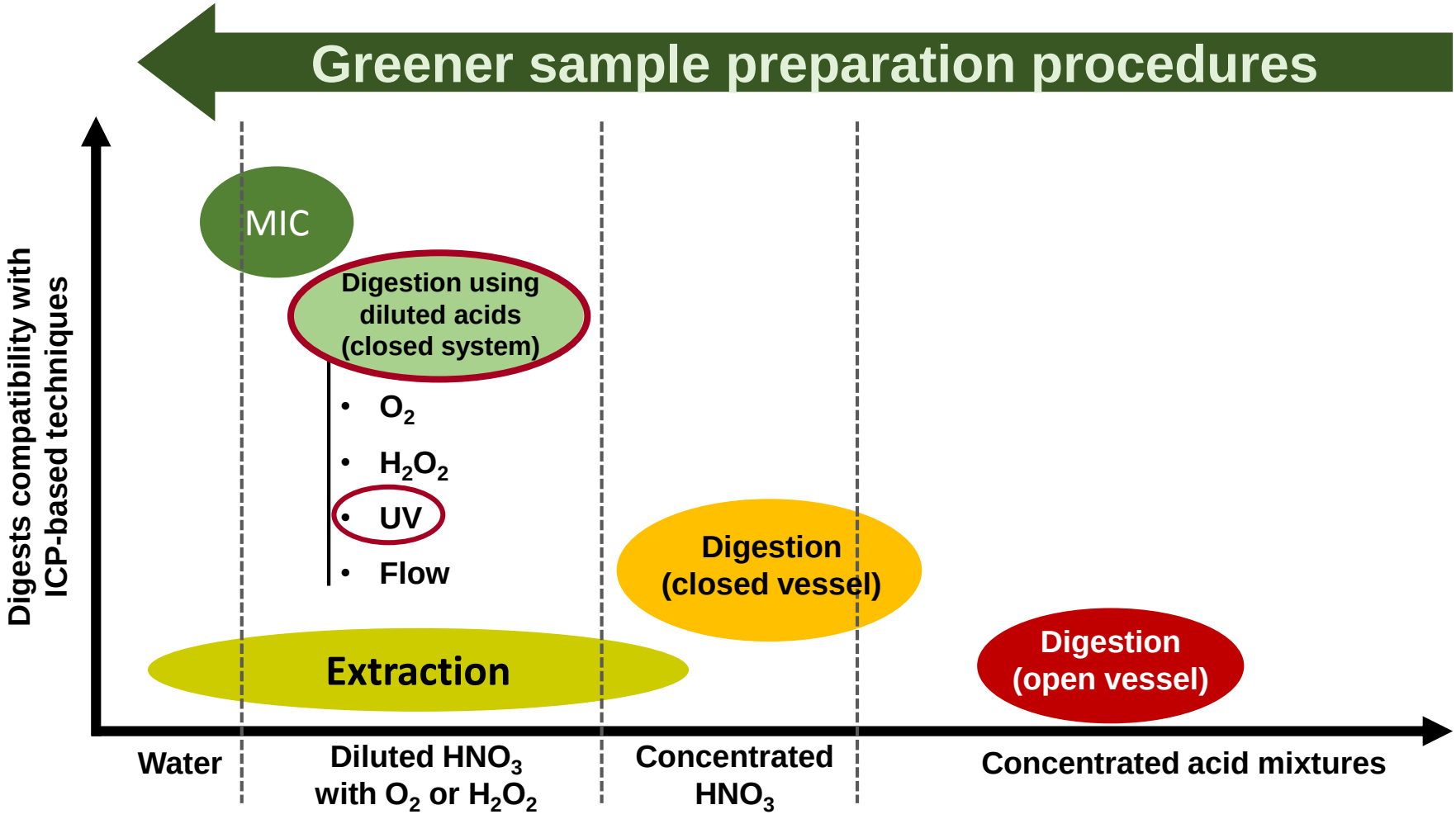
SAMPLE PRETREATMENT AND SEPARATION



MIC: Microwave-Induced Combustion
ICP: Inductively Coupled Plasma
UV: Ultraviolet

Adapted from: C. A. Bizzi et al. Journal Analytical Atomic Spectrometry 32 (2017) 1448-1466.

SAMPLE PRETREATMENT AND SEPARATION

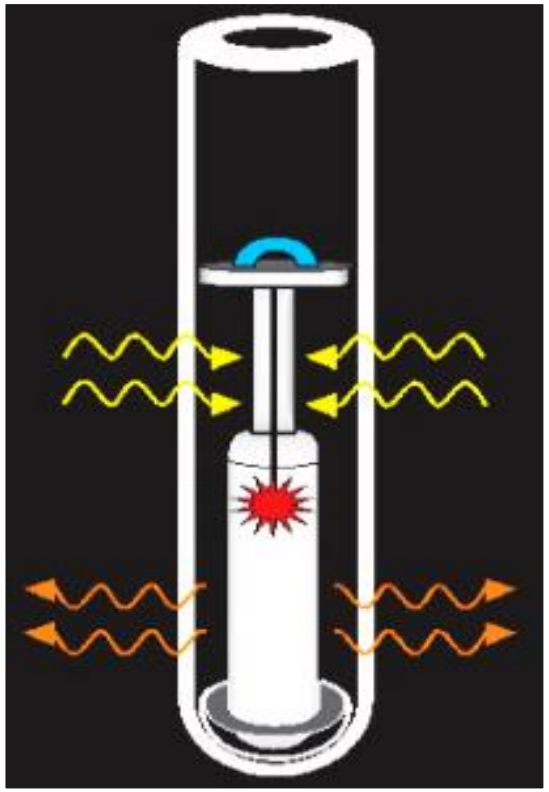


MIC: Microwave-Induced Combustion
ICP: Inductively Coupled Plasma
UV: Ultraviolet

OBJECTIVE

- To develop a single sample preparation method for polymeric e-waste digestion by microwave-assisted ultraviolet digestion (MAWD-UV)

- To use of diluted acids for further bromine and metals determination by inductively coupled plasma mass spectrometry (ICP-MS)



ELECTRONIC WASTE (E-Waste)

Sample preparation methods

MAWD-UV

Sample mass: 200 mg

Digestion mixture (15 mL):

A. HNO_3 (1 to 7 mol L^{-1})
B. HNO_3 + HCl (6 + 1, 3 + 0.5, 1.2 + 0.2 or 0.6 + 0.1 mol L^{-1})
C. 1 mol L^{-1} HNO_3 + H_2O_2 (0, 1.5, 3.5 or 4.7 mol L^{-1})
D. 0.5 mol L^{-1} HNO_3 + H_2O_2 (0, 1.5, 3.5, 4.7 or 5.3 mol L^{-1})
E. HNO_3 + HCl (0 + 0.5, 0.5 + 0.5, 0.5 + 1 or 0.5 + 0 mol L^{-1}) + 5.3 mol L^{-1} H_2O_2

Heating program:

i) 700 W for 40 min (ramp of 25 min)
Exhaustion at 125 m^3 air h^{-1}
ii) 0 W for 20 min for cooling
Exhaustion at 125 m^3 air h^{-1}
Max. pressure: 80 bar
Max. temperature: 250 °C

Dilution (25 mL)

MAWD

Sample mass: 200 mg

Digestion mixture (15 mL):

A. HNO_3 (1 to 7 mol L^{-1})
B. HNO_3 + HCl (6 + 1, 3 + 0.5, 1.2 + 0.2 or 0.6 + 0.1 mol L^{-1})

Heating program:

i) 700 W for 40 min (ramp of 25 min)
Exhaustion at 60 m^3 air h^{-1}
ii) 0 W for 20 min for cooling
Exhaustion at 125 m^3 air h^{-1}
Max. pressure: 80 bar
Max. temperature: 280 ºC

Dilution (25 mL)

Reference values

NAA for Br, Cr, and Sb

MAWD for Cd, Hg, and Pb

Sample mass: 200 mg

Digestion mixture (15 mL):

- 5 mL 14 mol L^{-1} HNO_3 + 1 mL 12 mol L^{-1} HCl

Heating program:

i) 1400 W for 35 min (ramp of 10 min)
Exhaustion at 60 m^3 air h^{-1}
ii) 0 W for 20 min for cooling
Exhaustion at 125 m^3 air h^{-1}
Max. pressure: 80 bar
Max. temperature: 280 ºC

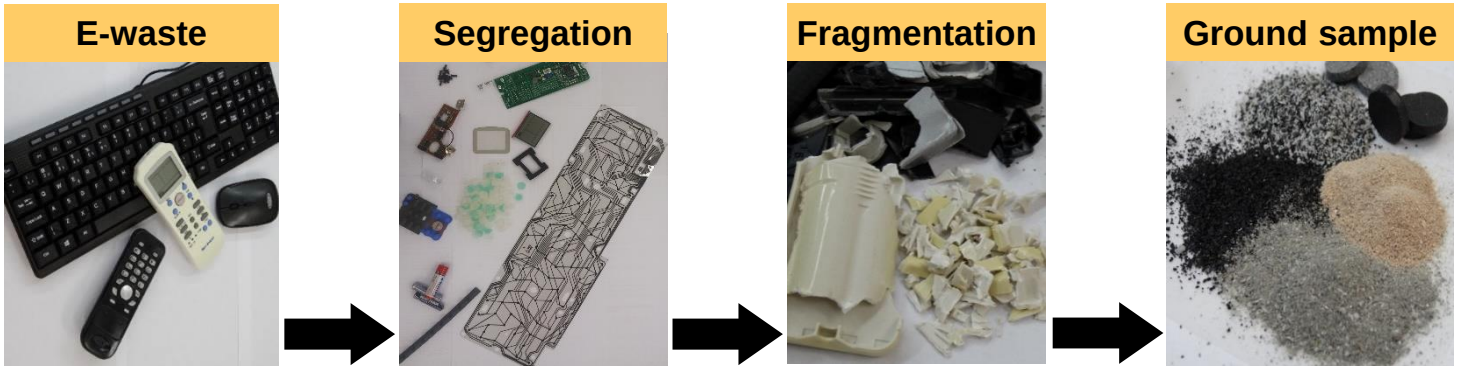
Determination of Br, Cd, Cr, Pb, and Sb by ICP-MS and Hg by FI-CVG-ICP-MS

Determination of Cd and Pb by ICP-MS and Hg by FI-CVG-ICP-MS

MAWD-UV: Microwave-Assisted Ultraviolet Digestion
MAWD: Microwave-assisted Wet Digestion
NAA: Neutron Activation Analysis
ICP-MS: Inductively Coupled Plasma Mass Spectrometry
FI-CVG-ICP-MS: Flow-Injection Cold Vapor Generation Inductively Coupled Plasma Mass Spectrometry

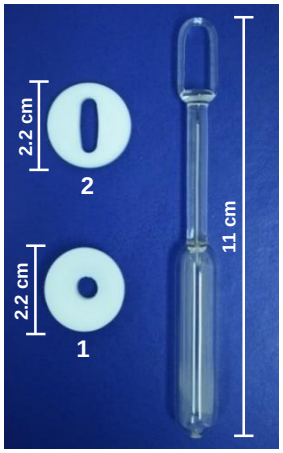
EXPERIMENTAL

Grinding polymeric parts with cryogenic mill

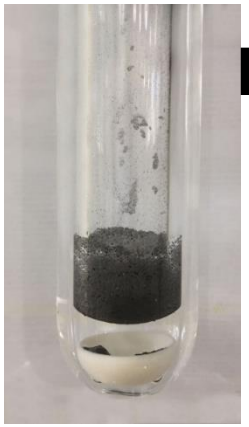


Cryogenic mil:
2 min of pre-cooling followed by 3 min for grinding
(last procedure repeated three times)

Microwave-assisted ultraviolet digestion (MAWD-UV)



UV lamp and PTFE devices
1- lamp base ring
2- lamp spacer



Lamp base ring, 5 mL of solution and 200 mg of sample

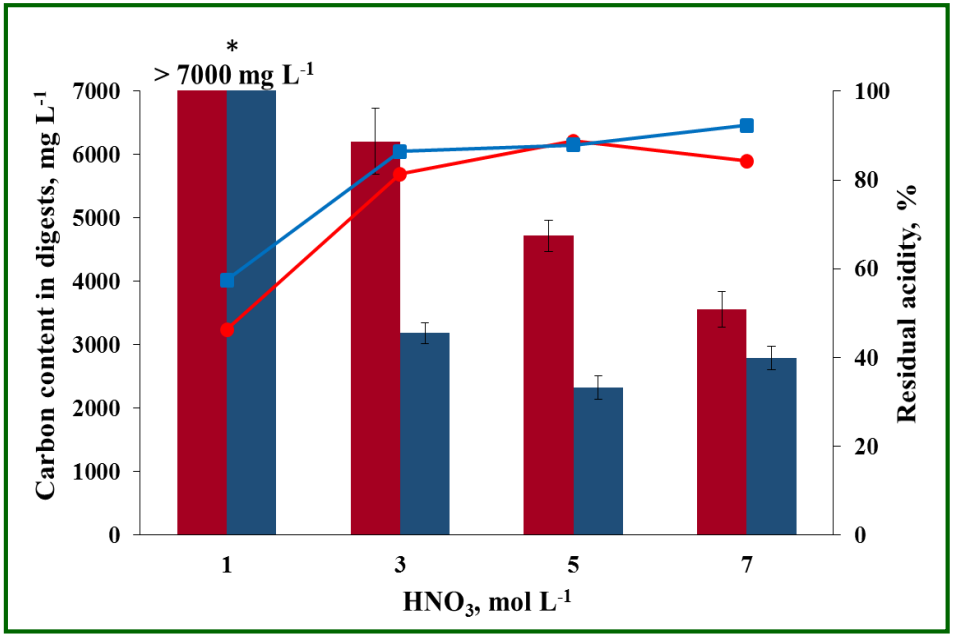
UV lamp with the lamp spacer

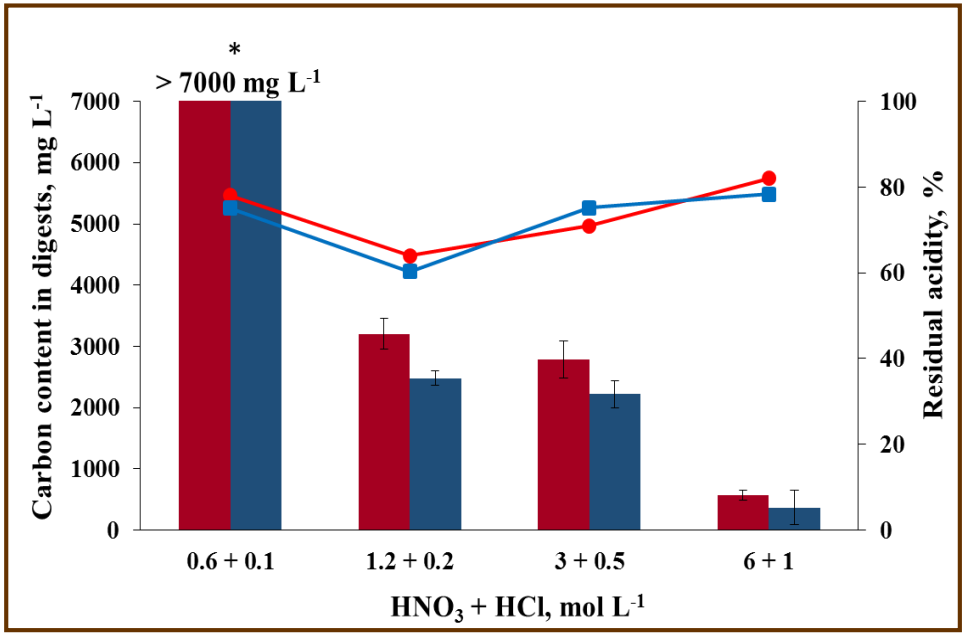
10 mL of solution (total volume: 15 mL)

MW irradiation

RESULTS

➢ Influence of UV radiation for e-waste digestion





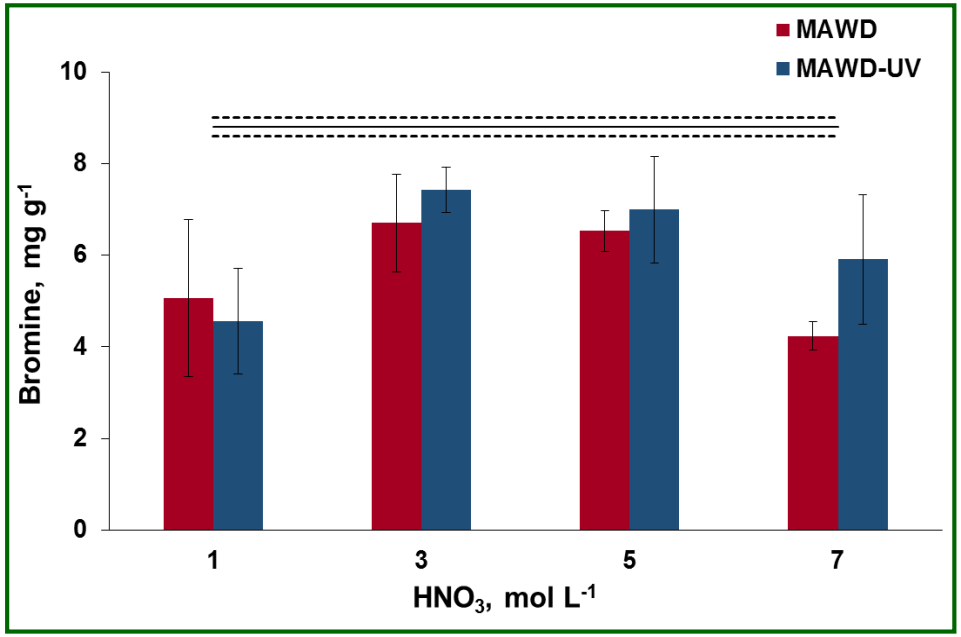
* Incomplete digestion

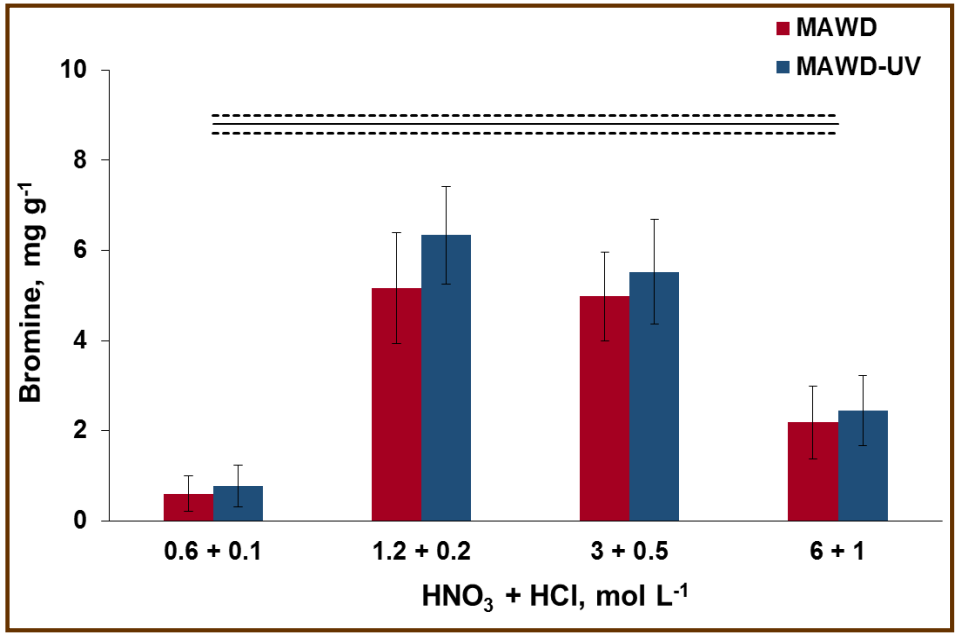
Improvement in digestion efficiency when more concentrated HNO_3 solutions and more concentrated HNO_3 + HCl mixtures were used

Digestion efficiency was more pronounced when the UV lamp was used

RESULTS

- **Influence of the digestion solution in MAWD-UV**
  - ***1 to 7 mol L^{-1} HNO_3 and mixtures of HNO_3 + HCl***





All conditions resulted in lower values for bromine in comparison with the reference value

UV lamp: improved the destruction of the organic matrix

RESULTS

➢ Influence of the digestion solution in MAWD-UV

- *Acid mixture with 5.3 mol L^{-1} H_2O_2*

Analyte	HNO_3 + HCl, mol L^{-1}				Reference value[a,b]
	0 + 0.5	0.5 + 0	0.5 + 0.5	0.5 + 1	
Br, mg g^{-1}	1.72 ± 0.19	8.32 ± 0.68	8.82 ± 0.67	5.76 ± 0.04	8.8 ± 0.2[a]
Cd, µg g^{-1}	8.16 ± 0.31	14.4 ± 1.2	16.0 ± 1.0	10.9 ± 0.1	15.8 ± 0.3[b]
Cr, µg g^{-1}	3.32 ± 0.37	3.02 ± 0.55	6.30 ± 0.70	5.45 ± 0.33	9 ± 1[a]
Hg[c], ng g^{-1}	62.0 ± 3.0	15.0 ± 1.0	66.2 ± 2.6	50.7 ± 4.3	65.9 ± 4.5[b]
Pb, µg g^{-1}	11.5 ± 0.8	25.1 ± 1.8	24.9 ± 1.4	21.4 ± 1.1	27.3 ± 2.6[b]
Sb, mg g^{-1}	2.17 ± 0.07	2.62 ± 0.26	2.99 ± 0.24	3.10 ± 0.32	3.27 ± 0.09[a]

[a] Results obtained by NAA.

[b] Results obtained after MAWD.

[c] Determination by FI-CVG-ICP-MS.

Considered as a compromise condition to provide quantitative recoveries

- Carbon content lower than 300 mg L^{-1}
- Residual acidity about 70%

⇨ Cr: no acid mixture was suitable for its quantitative recovery

Form of Cr present in the sample is important:

Use of extreme conditions for digestion (temperature and pressure)

RESULTS

Accuracy: CRM of low-density polyethylene (ERM 680k and ERM 681k)

Analyte	ERM EC680k		ERM EC681k	
	Found value	Certified value	Found value	Certified value
Br, μg g^{-1}	97 ± 8	96 ± 4	725 ± 71	770 ± 40
Cd, μg g^{-1}	18.3 ± 0.5	19.6 ± 1.4	132 ± 9	137 ± 4
Cr, μg g^{-1}	4.14 ± 0.27	20.2 ± 1.1	24.5 ± 6.1	100 ± 5
Hg*, μg g^{-1}	4.63 ± 0.22	4.64 ± 0.20	23.3 ± 0.6	23.7 ± 0.8
Pb, μg g^{-1}	12.5 ± 0.9	13.6 ± 0.5	91.2 ± 6.1	98 ± 6
Sb, μg g^{-1}	9.59 ± 0.19	10.1 ± 1.6	97.4 ± 8.0	99 ± 6

*** Determination by FI-CVG-ICP-MS**
Digestion of 200 mf of sample, n = 3.
Results for all elements by MAWD-UV were obtained using 15 mL of 0.5 mol L^{-1} HNO_3 + 0.5 mol L^{-1} HCl + 5.3 mol L^{-1} H_2O_2 for digestion.

No statistical difference in comparison with the certified values (*t*-test, 95% confidence level)

Spike recoveries → **From 90% (for Hg) to 113% (for Sb)**

CONCLUSION

- The developed method can be considered **environmental friendly**: use of diluted acid mixture, reduced time, less reagents consumption, and energy saving

- Possibility of using a **single protocol** for further Br and metals determination

ACKNOWLEDGEMENTS

Organizing Committee

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Funding Agencies

CNPq

CAPES

FAPERGS

SAMPLE PREPARATION STEP

Digestion efficiency

✓ **Residual acidity**

%, in relation to the initial amount of acid

✓ **Residual carbon content (RCC)**

%, in relation to the amount of C originally present in the sample

✓ **Carbon content in digests/Dissolved organic carbon (DOC)**

mg L^{-1}, dissolved carbon in final digests

Suitable digests: ↓ RA, RCC and DOC

Zischka, M. et al. Fresenius' Journal of Analytical Chemistry 361 (1998) 90-95.

Procedures for e-waste digestion

Sample preparation step

WET DIGESTION

Large consumption of reagents, time, and energy

↓

Non-environmentally sustainable aspects

EXTRACTION

Water-soluble species are extracted

↓

E-waste: Br is commonly present as organic molecules in polymers

↓

Poor extraction efficiency

MIC

Bromine and metals determination: two sample preparation procedures

Problem: there is no single protocol for bromine and metals

MIC: Microwave-Induced Combustion

Adapted from Flores, E. M. M., Microwave-assisted sample preparation for trace element determination, Elsevier, 2014.