

Characterization of Different Types of Biomass Wastes Using Thermogravimetric and ICP-MS Analyses

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The purpose of this study was to characterize some types of biomass wastes resulted from different activities such as: agriculture, forestry and food industry using thermogravimetric and ICP-MS analyses. Also, it was optimized an ICP-MS method for the determination of As, Cd and Pb from biomass ash samples. The ICP-MS analysis revealed that the highest concentration of metals (As, Cd, Pb) was recorded in the wood waste ash sample, also the thermogravimetric analysis indicated that the highest amount of ash was obtained for the same sample (26.82%). The biomass wastes mentioned in this study are alternative recyclable materials, reusable as pellets and briquettes.

Keywords: ash, biomass, ICP-MS, minor elements, TG

The valorisation of the biomass ashes as added-value materials for different productive sectors are essential from an economic and environmental perspective. The advantage of this process is reflected by reducing costs for biomass power producers and is favouring the development of a circular and sustainable economy [1-8]. Biomass ashes are the final products accumulating from the thermal combustion and gasification of biomass for heat and electricity production. The disposal of ashes in landfills is still a common practice in Romania, which causes considerable costs for the biomass-based power plants, with serious environmental problems. For this reasons it is necessary to find alternatives for recycling of the ashes from the combustion plants. [8, 9]. In the combustion process of the biomass fuels, the inorganic part is oxidized, volatilized and calcinated. At incineration temperatures above 600°C, the release CO₂ will take place at the same time as the release of other volatile inorganic compounds such as sodium and potassium compounds. The use of biomass fuels for power generation leads to atmospheric emissions and produces solid wastes that concentrate metals and other elements from the original feedstock [10-13].

Determination of trace metals in ashes generally include a mineral acid extraction (wet oxidation) followed by atomic absorption (AAS) or inductively coupled plasma mass spectrometry (ICP-MS) analyses. Wet oxidation is normally carried out by digestion of the sample in a mixture of strong acids such as sulphuric, hydrochloric, hydrofluoric, nitric and perchloric acids. The way in which the ash sample is prepared from the biomass is therefore crucial for obtaining reliable and reproducible results [13-15].

The excessive accumulation of toxic metals such as As, Cd, Pb in some biomass waste presents a risk for human health. Regarding metals, cadmium having the most hazardous long-term effects on human health. Due to environmental pollution with heavy metals coming from industrial activity, various types of biomass wastes contain these pollutants in their compositions [14, 16].

The information of the thermogravimetric analysis and the contents of metals are very important in combustion processes. It is desired to obtain a small amount of ash in the combustion process for the elimination of clogging ashes in the combustion plant. The biomass wastes are complex matrices containing in most cases over 75% carbohydrates. The ashes content after thermogravimetric analysis has in its composition CaO and CaCO₃ [16, 17].

The purpose of the study was to characterize some biomass waste samples using thermogravimetric analysis, in order to indicate additional data for the valorisation process and to establish an optimal method of determination for toxic elements (As, Cd and Pb) from the biomass wastes.

Experimental part

In study were selected and analysed three types of biomass wastes such as: S1-vegetable waste from food industry; S2 - wood waste from forestry; S3- vegetable waste from farming.

The samples were dried at 105°C and crushed less than 1mm. The moisture content was approximately 3 % – 3.7% for all the analysed samples.

Before metal analysis a calcination process was applied, the biomass samples were thermal treated with two different methods, such as: calcination at 550°C (method I), respectively at 820°C (method II) for 1h in a calcination oven.

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Materials

All the chemicals were of analytical reagent grade (Merck quality). Ultrapure water was produced with a Millipore Milli-Q System. For the calibration curves were prepared standards in the range 20 to 100 µg/L using a 1000 mg/L Multielement Certified Reference Material (ICP multielement standard solution XXI, Certipur, Merck). Quality control of the analytical results was performed with a multielement Certified Reference Material for ICP, 100 mg/L, Merck quality.

Equipment

Microwave Digestion System Ethos Up Milestone
ICP-MS type 7900 Agilent with Mass Hunter 4.4 software
Thermogravimetric analyser TG Netzsch STA 409
Millipore Milli-Q System
Calcination oven type Memmert UF 110

Analytical method

(i) Digestion procedure

0.5 gram of ash sample was introduced into the digestion cell and 10 ml of nitric acid (65%) was added. After the digestion was completed, solution from the digestion cell was filtered through filter paper (porosity 0.45µm) and brought to a volume of 25 mL, then the samples were analysed by ICP-MS equipment. The ash samples obtained with both calcination methods were treated in same conditions.

The digestion of samples was performed with a Microwave Digestion System Ethos Up Milestone following a program presented in Table 1.

Table 1
DIGESTION PROGRAM

Step	T1°C	T2°C	Power (W)	Time (min)
1	120	100	1400	15
2	120	100	1400	15
3	cooled	cooled	-	30

(ii) Metal analysis

The metal (As, Cd, Pb) concentrations were determined using a mass spectrometer with coupled plasma (ICP-MS) type 7900 Agilent with Mass Hunter 4.4 software. The ICP-MS operating parameters are presented in Table 2.

Table 2
SPECTROMETER OPERATING PARAMETERS

<i>ICP-MS spectrometer parameters</i>	
Delay time: 60s	Purge gas flow: normal
Replicates: 3 times	Peristaltic pump: 1,5mL/min
<i>Tune parameters</i>	
<i>Plasma parameters</i>	
Plasma flow rate: 15L/min	Power RF: 1550W
Auxiliary flow rate: 0,90L/min	Plasma view: axial
Nebulizer Pump: 0,10rps	RF matching 1,30V
<i>Plasma mode</i>	
Plasma Mode: General Purpose	Sample Depth: 10 mm
<i>Cell parameters</i>	
He Flow: 4,3mL/min	OctpBias: -8.0 V
<i>Spectral peak processing</i>	
Peak algorithm: Peak area	Peak pattern: 3 points
Replicates: 3	Integration time: 0,2001 sec.
<i>Sample acquisition</i>	
Sample uptake: 30 sec.	Stabilize: 40 sec.
<i>Post run</i>	
Probe rinse (Sample): 10 sec.	Probe rinse (Standard): 10sec.

The in-house validation of the analytical method applied was performed in order to evaluate the performance parameters of the method: limit of detection LOD, limit of quantitation LOQ, repeatability, intermediate precision, expanded uncertainty and recovery. The experimental studies (table 3) were applied on S2 sample due to high content of metals.

Table 3
“IN-HOUSE” VALIDATION EXPERIMENTS

Parameters	Experiments
LOQ and LOD	5 independent fortified blank solutions (3 µg/L)
Repeatability	10 independent standard solution of 20µg/L concentration
Intermediate precision	4 experiments (3 standard solution per experiment analysed by 2 chemists in 4 different days), 12 independent standard solution of 20 µg/L
Recovery	10 independent fortified sample solutions (25 µg/L)

The expanded uncertainty of the analytical results was estimating using following formula [18]:

$$U_{expanded} = k * U_{combined} \quad (1)$$

$$U_{expanded} = k * \sqrt{(U_c^2 + U_v^2 + U_{rep}^2 + \frac{1}{U_{mas}}^2 + \frac{1}{U_{rec}}^2)} \quad (2)$$

where k is a coverage factor; value 2 for 95% confidence level;

$U_{combined}$ – combined standard uncertainty; U_c – concentration uncertainty (instrument calibration, flasks, pipettes, reference standard material); U_v – 50-ml volumetric flask (calibration, temperature); U_{rep} – repeatability uncertainty (mass, volume, concentration, extraction recovery); U_{mass} – weight uncertainty (balance calibration, linearity);

U_{rec} – extraction recovery uncertainty.

(iii) TG analysis

To evaluate the structural characterization and behaviour of the biomass waste it was use a thermogravimetric analyser Netzsch STA 409, TG operating parameters being presented in table 4, while the mass transformation during the thermogravimetric analyses is presented in table 5.

Table 4
THERMOGRAVIMETRIC OPERATING PARAMETERS

Parameters	Settings
Temperature range	100°C-1000°C
Average flow rate (Argon- Carrier gas)	60ml/min
Average flow rate (Synthetic gas – Reaction gas)	20ml/min
Heating value	10°C/min

Table 5
THE SUCCESSIVE STEPS OF THERMAL DEGRADATION PROCESS [1]

Step	Mass transformation during the TG analysis	Temperature [°C]
1	Moisture removal	100-180°C
2	Decomposition of carbohydrates	180-270°C
3	Decomposition of proteins	320-450°C
4	Decomposition of volatile substances and the carbonates	>500°C
5	Char decomposition, responsible for the late formation of H ₂ and CO.	>750°C

Results and discussions

Thermogravimetric analyses

Thermogravimetric analysis describes the processes of decomposition of matter under the influence of temperature. At the end of TG analysis, it is known the temperature where the sample was decomposed and the ash content obtained for each samples.

In the study, the biomass wastes undergoes various transformations of weight depending on their chemical composition: processes of dehydration, carbonization and combustion [1], the changes of waste's weight being described in Figures 1-3.

The degradation thermal step is influenced by temperature and the chemical composition of the biomass wastes.

The TG analysis of S1 sample (vegetable waste from food industry) is presented in Figure 1, the mass transformation during the analysis being presented in table 7.

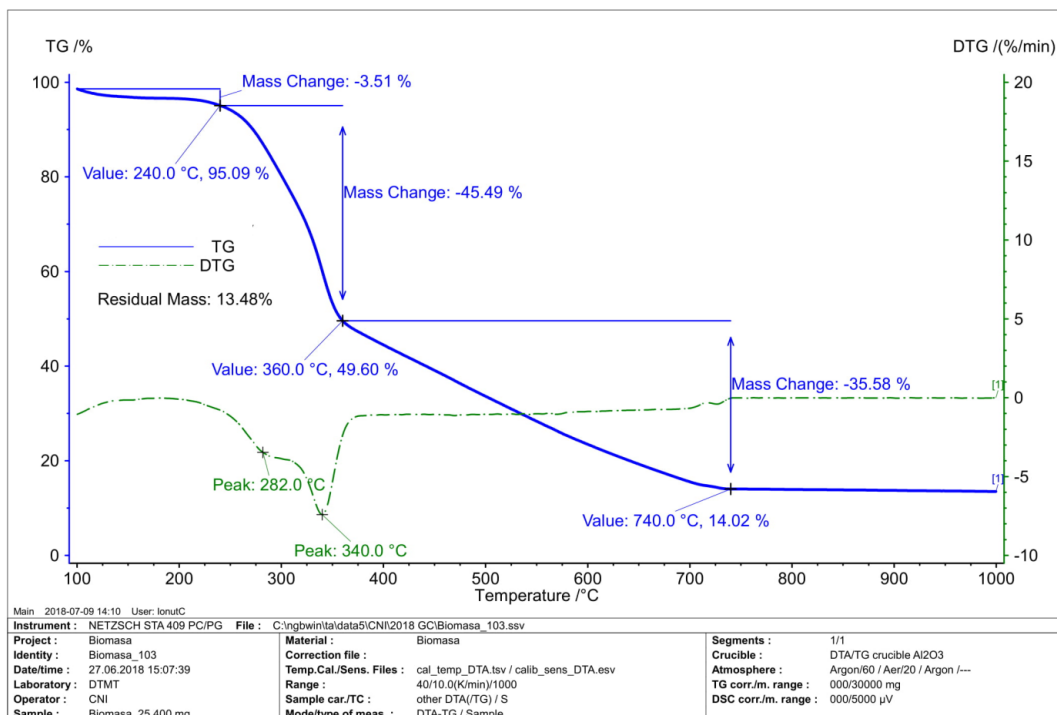


Fig. 1. Thermogravimetric analysis of the sample S1

Table 6
MASS TRANSFORMATION DURING THE TG ANALYSIS FOR S1 SAMPLE

Step	Process	Results [%]	Temperature [°C]
1	Decomposition of carbohydrates	3.51	250°C
2	Decomposition of proteins	45.49	340°C
3	Decomposition of volatile substances and the carbonates	35.58	740°C

The residual mass (ash) left in the alumina crucible at the end of the assay was 13.48% (Figure 1). Complex matrix of vegetable waste from food industry is composed from: peel potatoes, peel tomatoes, scrap processing vegetables etc. This complex matrix contains volatile substances and carbohydrates which decompose as it can see in Table 6.

The TG analyze of the S2 sample (wood waste from forestry) is presented in Figure 2. The wood waste from forestry contain: sawdust from woodworking, sawdust from wood, woody debris, branches, bark etc. The thermal degradation process for S2 sample is presented in Table 8.

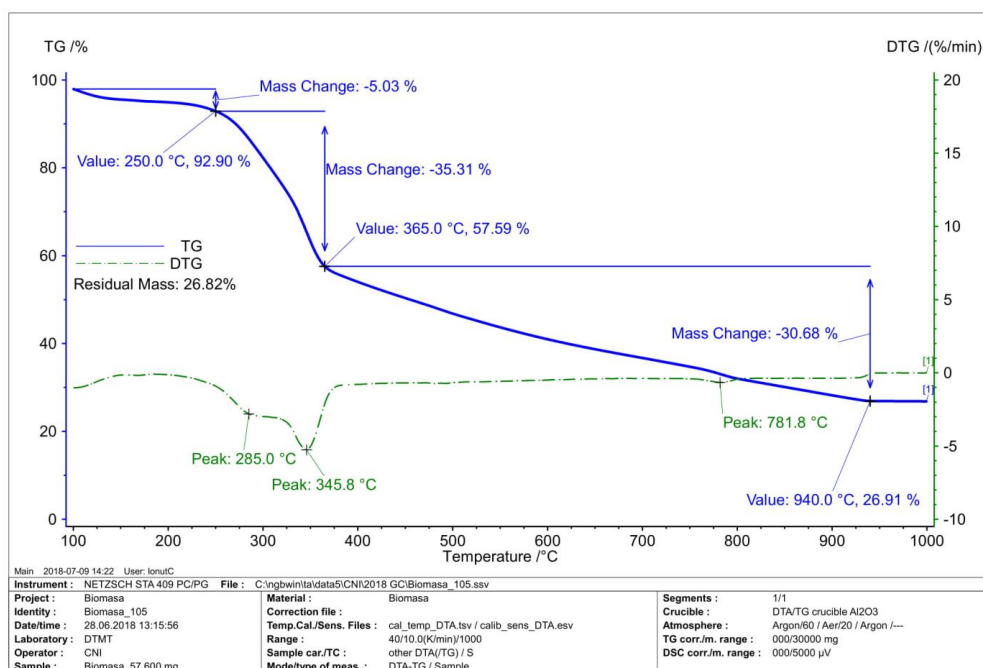


Fig. 2. Thermogravimetric analysis of the sample S2

Table 7
MASS TRANSFORMATION DURING THE TG ANALYSIS FOR S2 SAMPLE

Step	Process	Results [%]	Temperature [°C]
1	Decomposition of carbohydrates	5.03	250°C
2	Decomposition of proteins	35.3	356°C
3	Decomposition of volatile substances and the carbonates	30.68	781,8°C
4	Char decomposition	26.91	940°C

The residual mass (ash) was 26.82% (Figure 2). After the decomposition of volatile substances and the carbonates, the S2 sample still has a high decomposition char of approximately 27% at 940°C (table 7).

The TG analyze for the S3 sample (vegetable waste from farming) is presented in Figure 3. The S3 sample is composed from fruits and vegetables wastes.

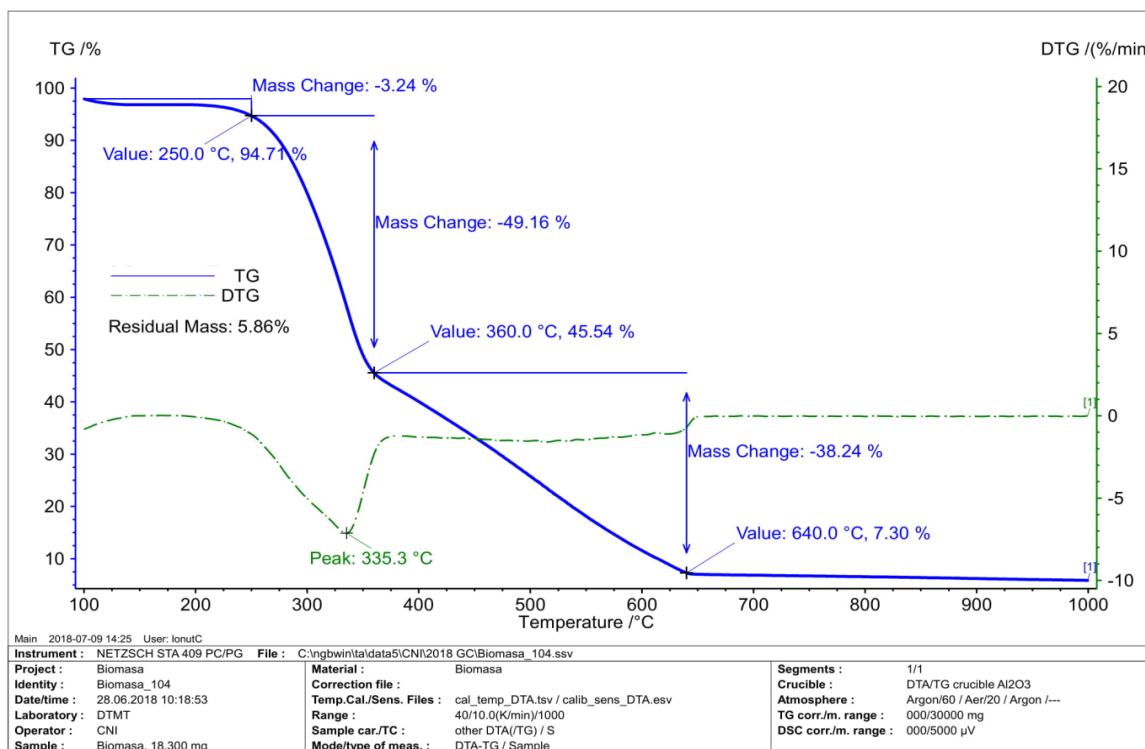


Fig. 3. Thermogravimetric analysis of the sample S3

Table 8
MASS TRANSFORMATION DURING THE TG ANALYSIS FOR S3 SAMPLE

Step	Process	Results [%]	Temperature [°C]
1	Decomposition of carbohydrates	3.24	250°C
2	Decomposition of proteins	45.54	360°C
3	Decomposition of volatile substances and the carbonates	7.30	640°C

The main constituents of the biomass wastes are: cellulose, hemicellulose and lignin.

The wood waste from forestry decomposes more slowly than vegetable waste from food industry and vegetable waste from farming, as it can see in the table 6 to 8.

From the table 7 it can be concluded that the S2 sample contains 97.92% solid material that must decomposed under the thermal treatment. The amount of ash resulting from thermogravimetric analysis for the three samples analysed decreases in the following order of: S2 (26.82%)> S1 (13.48%)> S3 (5.86%).

The measurement results for TG analysis show high volatile content (35.58%) for S1 sample and low volatile content (7.30%) for S3 sample. The S2 sample presents 30.68% volatile substances as it can see in table 7. Thermal analysis has shown to be a powerful tool for investigating the thermal degradation processes from our biomass wastes.

If we know the behaviour of the biomass waste under the thermal degradation process, we could estimate the amount of pellets or briquettes that are necessary to heat a home. From the residual ash of our biomass wastes sample we could estimate the quantity of metals that remains after the combustion step. These processes are highly important, given the risk of fouling and ash slagging on the walls of home heated surfaces.

Determination of the As, Cd, Pb in the biomass ash

In table 9 are presented the values of performance parameters obtained in in-house validation experiments using applied analytical method (ICP-MS technique). The results of As, Cd and Pb for both thermal treated methods are indicated in Figure 4.

Table 9
PERFORMANCE PARAMETERS OF AS, CD AND PB USING ICP-MS TECHNIQUE

Metals	LOD (mg/Kg)	LOQ (mg/Kg)	Acuracy (mg/Kg)	RSD _r * (%)	RSD _{Ri} ** (%)	U _{ex} *** (%)	Recovery (%)
As	0.04	0.15	0.05	0.64	2.14	17.67	84
Cd	0.06	0.19	0.13	0.61	1.92	18.33	90
Pb	0.08	0.27	0.06	0.81	1.95	16.52	92

*Repeatability; **Intermediate precision; ***Measurement uncertainty

The differences between three biomass wastes include the moisture content and chemical composition of the biomass ash wastes, which will have a potential effect on the plant combustion efficiency. The biomass coming from the wood waste has small moisture content (2.95%), but high content of metals. This type of biomass waste could be a promising materials for the future valorisation as pellets or briquettes for combustion plant, but also for domestic use.

The content of metals in biomass ash is variable and depends on the type and origin of biomass, harvesting time, sampling technique, transport and storage.

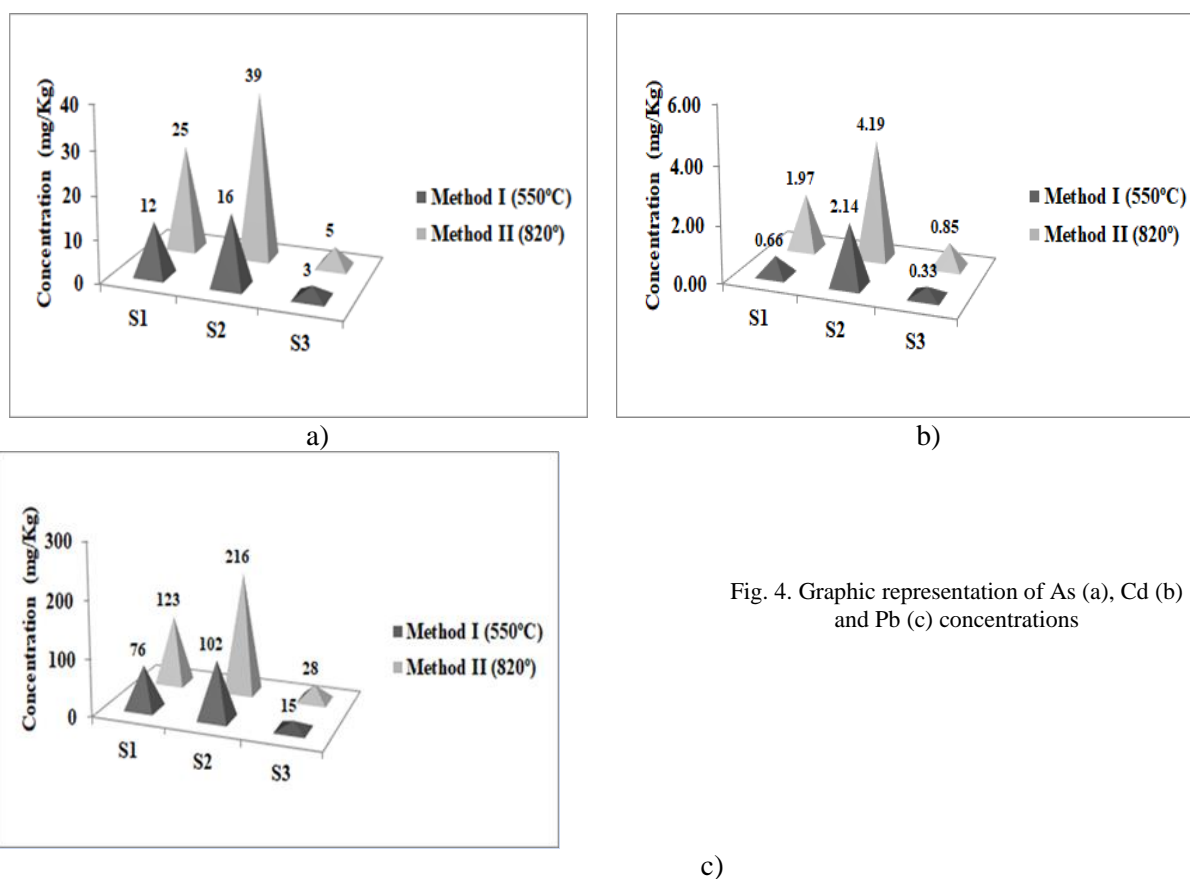


Fig. 4. Graphic representation of As (a), Cd (b) and Pb (c) concentrations

In the S2 sample ash it was obtained a higher metal concentrations compared to the other two samples as shown in Figure 4a) and b). As it could be observed in Figure 4a) the arsenic highlighted a higher concentration for the S2 ash sample. In figure 4c), the lead highlighted a higher concentration for the S2 sample coming from the wood waste. The results obtained using calcination method II conduct to higher concentration of metals for all samples.

Conclusions

The content of toxic elements As, Cd and Pb was determined in three biomass waste samples resulted from different activity sectors from Romania. The decomposition of biomass waste using TG analysis and the amount of the ash gives us valuable information reusable biomass wastes, being potential materials for valorisation as pellets or briquettes.

Biomass sample calcination at 550°C can give inaccurate results from ICP-MS analysis as result of significant unburned carbon content, retained in the ash mass. Processing the sample at a temperature of 820°C produces an ash composition more suitable for ICP-MS analysis. Good and reproducible results were obtained follow method II (820°C) for all the toxic elements analysed. The biomass waste indicate for S2 sample highest concentration of metals and ash content. The recovery percentage were higher that 84%, the highest recovery yields (>90%) was obtained for cadmium and lead.

As a conclusion, method calcination at 820°C is suitable for the characterization of the toxic elements As, Cd and Pb from the biomass wastes.

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