

# Thermal behavior of malonic acid, sodium malonate and its compounds with some bivalent transition metal ions in dynamic N<sub>2</sub> and CO<sub>2</sub> atmospheres

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## Abstract

Thermal stability and thermal decomposition of malonic acid, sodium malonate and its compounds with Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) were investigated employing simultaneous thermogravimetry and differential thermal analysis (TG-DTA), differential scanning calorimetry (DSC) in N<sub>2</sub> and CO<sub>2</sub> atmospheres and TG-FTIR in N<sub>2</sub> atmosphere. The thermal decomposition of malonic acid occurs with decarboxylation followed by the formation of acetic acid in both atmospheres. For sodium malonate the thermal decomposition occurs with formation of sodium carbonate, and for the transition metal malonates the final residue was: MnO (N<sub>2</sub>, CO<sub>2</sub>), FeO (N<sub>2</sub>), Fe<sub>3</sub>O<sub>4</sub> (CO<sub>2</sub>), Co + CoO (N<sub>2</sub>), CoO (CO<sub>2</sub>), Ni (N<sub>2</sub>, CO<sub>2</sub>), Cu (N<sub>2</sub>, CO<sub>2</sub>) and ZnO (N<sub>2</sub>, CO<sub>2</sub>).

**Keywords:** bivalent transition metals; malonate; thermal behavior.

## 1. Introduction

Several investigations have been carried out on the thermal behavior of metal malonates in various atmospheres. The papers published are concerned with the thermal decomposition of bivalent transition metal malonates in various atmospheres[1], thermal behavior of dicarboxylic acid in Ar, CO<sub>2</sub> and air atmospheres[2], non-isothermal decompositions of nickel malonate dihydrate and of nickel hydrogen malonate dehydrate in N<sub>2</sub>, H<sub>2</sub> and air atmospheres[3], non-isothermal decomposition of cobalt malonate dehydrate and cobalt hydrogen malonate dehydrate in N<sub>2</sub>, H<sub>2</sub> and air atmospheres[4], the comparative study of the thermal decomposition of copper(II) and zinc(II) malonate, maleate and succinate complexes using direct current electrical conductivity measurements using static air and dynamic dry nitrogen atmospheres[5] and isothermal and non-isothermal decomposition of zinc malonate dehydrate under vacuum, in N<sub>2</sub>, H<sub>2</sub> and air atmospheres[6]. As continuation of our previous study on thermal behavior of malonic acid, sodium malonate and its compounds with some bivalent transition metal ions in air atmosphere[7], this paper deals with the thermal behavior and thermal decomposition of these compounds in dynamic N<sub>2</sub> and CO<sub>2</sub> atmospheres.

## 2. Experimental

The preparation, elemental analysis and X-ray powder diffraction patterns of the metal malonates were described in the previous paper[7]. Simultaneous TG-DTA and DSC curves were obtained with two thermal analysis systems, model SDT 2960 and DSC Q10, both from TA

Instruments. The purge gas was N<sub>2</sub> and CO<sub>2</sub> flow of 100 mL min<sup>-1</sup> for TG-DTA and 50 mL min<sup>-1</sup> for DSC experiments. A heating rate of 20 °C min<sup>-1</sup> was adopted, with samples weighing about 7 mg for TG-DTA and 2 mg for DSC. Alumina and aluminum crucibles, the latter with perforated cover, were used for TG-DTA and DSC, respectively.

The measurements of the gaseous products were carried out using a Thermogravimetric Analyzer Mettler TG-DTA coupled to a Fourier-transform infrared (FTIR) Nicolet iS10 spectrometer with gas cell and DTGS KBr detector. The furnace and the heated gas cell (250 °C) were coupled through a heated (T = 200 °C) 120 cm stainless steel line transfer with diameter 3 mm both purged with dry nitrogen (50 mL min<sup>-1</sup>). The FTIR spectra were recorded with 32 scans per spectrum at a resolution of 4 cm<sup>-1</sup>.

## 3. Results and Discussion

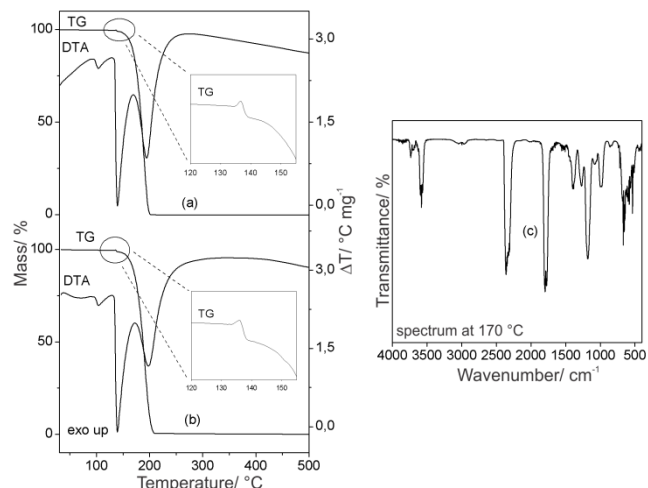
### 3.1. Malonic acid

The simultaneous TG-DTA curves of malonic acid in N<sub>2</sub> and CO<sub>2</sub> atmospheres are shown in Fig. 1a and b, respectively. In both atmospheres the TG curve shows mass loss in a single step between 140 – 210 °C, with total mass loss and the DTA curve exhibits three endothermic peaks. The first endothermic peak at 103 °C (N<sub>2</sub>) or 104 °C (CO<sub>2</sub>) is due to solid phase transition, which was confirmed by X-ray powder diffraction as already observed in the thermal decomposition in an air atmosphere[7]. The second and third endothermic peaks at 140 °C and 194 °C (N<sub>2</sub>) or 139 °C and 198 °C (CO<sub>2</sub>) are attributed to the melting and thermal decomposition of malonic acid, respectively. The thermal decomposition of this acid in both atmospheres occurs with decarboxylation followed by the formation of acetic acid

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which was monitored and identified mostly on base of their FTIR reference available NICOLET libraries, as shown in Fig. 1c. The small discontinuity observed in the TG curve in both atmospheres during the melting of the malonic acid is attributed to the particle size and/or the equipment used (SDT 2960 – TA Instruments). No discontinuity is observed in the TG curves obtained in the same equipment with sample after pulverization or in METTLER equipment with sample without pulverization.

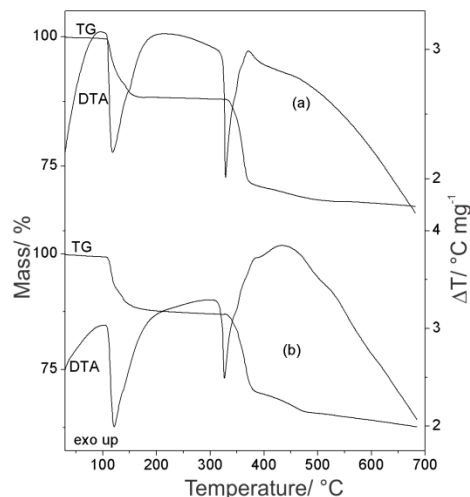


**Figure 1.** Simultaneous TG-DTA curves in dynamic (a)  $N_2$  ( $m = 7.116$  mg), (b)  $CO_2$  (7.132) atmospheres and (c) IR spectrum of the gases released during the decomposition of malonic acid in  $N_2$  atmospheres.

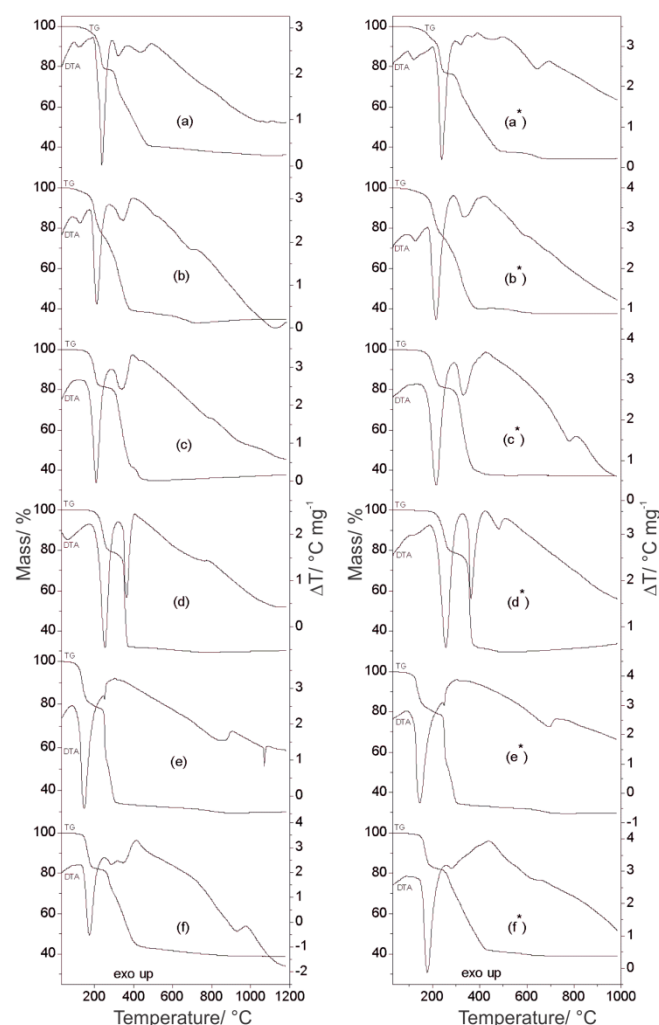
The TG-DTA curves in  $N_2$  and  $CO_2$  atmospheres showed the same results than that in air atmosphere [7], showing that the thermal decomposition mechanism of the malonic acid is independent of the atmosphere used.

### 3.2. Sodium malonate monohydrate

For the sodium malonate monohydrate the TG-DTA curves in  $N_2$  and  $CO_2$  atmospheres are shown in Fig. 2a and b, respectively. These curves show mass losses in four steps and thermal events corresponding to these losses or due to physical phenomenon. The first mass loss between 105 – 170 °C ( $N_2$ ) or 105 – 180 °C ( $CO_2$ ) corresponding to an endothermic peak at 120 °C ( $N_2$ ) or 122 °C ( $CO_2$ ) is due to dehydration. In both atmospheres the anhydrous compound is stable up to 327 °C and above this temperature the thermal decomposition occurs in three steps between 327 – 380 °C, 380 – 510 °C and 510 → 675 °C ( $N_2$ ) or 327 – 385 °C, 385 – 485 °C and 485 – >700 °C ( $CO_2$ ) with losses of 16.75%, 3.00% and 1.34% ( $N_2$ ) or 17.62%, 4.52% and 3.07% ( $CO_2$ ) respectively, without thermal events in the  $N_2$  atmosphere or evidence of exothermic event between 350 and 500 °C ( $CO_2$ ), attributed to the pyrolysis of the compound and carbonaceous residue with formation of sodium carbonate. In both atmospheres, the endothermic peak at 327 °C is due to the melting of the compound.



**Figure 2.** Simultaneous TG-DTA curves of the sodium malonate in (a)  $N_2$  (7.069 mg) and (b)  $CO_2$  (7.084 mg), atmospheres.



**Figure 3.** TG-DTA curves of the compounds in dynamic  $N_2$  and  $CO_2^*$  atmospheres: (a, a\*)  $MnL \cdot 2.5H_2O$  ( $m = 7.126$  mg; 7.024 mg \*), (b, b\*)  $FeL \cdot 2.5H_2O$  ( $m = 7.145$  mg; 7.009 mg\*), (c, c\*)  $CoL \cdot 2H_2O$  ( $m = 7.089$  mg; 7.242 mg\*), (d, d\*)  $NiL \cdot 2H_2O$  ( $m = 7.148$  mg; 7.182 mg\*), (e, e\*)  $CuL \cdot 2H_2O$  ( $m = 7.079$  mg; 7.329 mg\*) and (f, f\*)  $ZnL \cdot 2H_2O$  ( $m = 7.295$ mg; 7.085 mg\*).

### 3.3. Transition metal malonates

#### 3.3.1. TG-DTA Curves

The simultaneous TG-DTA curves of the bivalent transition metal malonates obtained in nitrogen and carbon dioxide are shown in Fig. 3. These curves show mass losses or gain in two, three or four steps, corresponding to endothermic peaks due to dehydration or pyrolysis of the anhydrous compounds.

The thermal stability of the hydrated (I) or anhydrous (II) compounds in both atmospheres as shown by the TG – DTA curves depend on the nature of the metal ion and they follow the order:

I: Ni > Co > Mn = Zn > Fe > Cu

II: Ni > Mn > Co > Fe > Zn > Cu

For each compound a great similarity is noted concerning the TG – DTA profiles in both atmospheres around 400 °C and above this temperature the thermal decomposition depend on the nature of the purge gas used and so the features of each of these compounds are discussed individually.

**Manganese Compound.** The simultaneous TG – DTA curves in N<sub>2</sub> and CO<sub>2</sub> atmospheres are shown in Fig. 3a and a\*, respectively. The first mass loss between 105-250 °C (N<sub>2</sub>) or 105 -255 (CO<sub>2</sub>), that begin through a slow process followed by a fast one, corresponding to the endothermic peaks at 130 and 235 °C (N<sub>2</sub>) or 130 and 240 °C (CO<sub>2</sub>) is due to dehydration with loss of 2.5H<sub>2</sub>O (Calcd. = 22.32%, TG = 22.19% (N<sub>2</sub>), 22.74% (CO<sub>2</sub>)).

For the thermal decomposition of the anhydrous compound, the TG curve shows mass losses in two steps between 280 - 1035 °C (N<sub>2</sub>) or 280 – 680 °C (CO<sub>2</sub>). In spite of the DTA curve suggests that the first mass loss occurs through overlapping steps, these are two (N<sub>2</sub>) or three (CO<sub>2</sub>). The first mass loss between 280 and 485 °C (N<sub>2</sub>) or 280 – 495 °C (CO<sub>2</sub>), corresponding to the endothermic peaks at 325 °C and 440 °C (N<sub>2</sub>) and 325, 380 and 460 °C (CO<sub>2</sub>) with loss of 38.05% (N<sub>2</sub>) and 39.53% (CO<sub>2</sub>) is attributed to the pyrolysis of the compound with formation of mixture of manganese oxide (Mn<sub>x</sub>O<sub>y</sub>) and carbonaceous residue (N<sub>2</sub>) and Mn<sub>3</sub>O<sub>4</sub>(CO<sub>2</sub>) (Calcd. = 62.74%, TG = 62.27% (CO<sub>2</sub>)).

The last step observed between 485 – 1035 °C (N<sub>2</sub>) without any thermal event, with loss of 4.52% is attributed to the pyrolysis of carbonaceous residue together with partial reduction reaction of Mn<sub>x</sub>O<sub>y</sub> to MnO (Calcd. = 64.89%, TG = 64.76%). In this step no thermal event is observed, probably because the pyrolysis of the carbonaceous residue occurs slowly and the heat evolved in this step is insufficient to produce a thermal event. The small endothermic peak at 1080 °C is attributed to the reduction reaction of remaining Mn<sub>x</sub>O<sub>y</sub> to MnO. For the CO<sub>2</sub> atmosphere the last step between 580 – 690 °C, corresponding to an endothermic peak at 650 °C, with loss of 2.49% is attributed to the reduction reaction of Mn<sub>3</sub>O<sub>4</sub> to MnO (Calcd. = 2.60%; TG = 2.49%).

**Iron Compound.** The simultaneous TG – DTA curves in N<sub>2</sub> and CO<sub>2</sub> atmospheres are shown in Fig. 3b and b\*, respectively. The first mass loss between 80 and 225 °C, that

begins through a slow process followed by a fast one in both atmospheres, corresponding to the endothermic peaks at 125 and 210 °C (N<sub>2</sub>) or 130 and 215 °C (CO<sub>2</sub>) is due to dehydration with loss of 2.5H<sub>2</sub>O (Calcd. = 22.30%, TG = 21.92% (N<sub>2</sub>), 21.65% (CO<sub>2</sub>)).

Immediately after the dehydration, the anhydrous compound shows mass losses in two steps up to 715 °C (N<sub>2</sub>) and 690 °C (CO<sub>2</sub>). The first mass loss between 225 – 390 °C (N<sub>2</sub>) and 225 – 400 °C (CO<sub>2</sub>), corresponding to the endothermic peak at 350 °C (N<sub>2</sub>) or 335 °C (CO<sub>2</sub>) with loss of 38.35% (N<sub>2</sub>) and 38.29% (CO<sub>2</sub>) is attributed to the pyrolysis of the compound with formation a mixture of iron oxide, Fe<sub>x</sub>O<sub>y</sub>, and carbonaceous residue. The last mass loss between 390 – 715 °C (N<sub>2</sub>) and 500 – 690 °C (CO<sub>2</sub>) corresponding to the endothermic peak at 700 °C (N<sub>2</sub>) and 590 °C (CO<sub>2</sub>) with loss of 6.61% (N<sub>2</sub>) and 2.31% (CO<sub>2</sub>) is attributed to the pyrolysis of the carbonaceous residue and reduction reaction of Fe<sub>x</sub>O<sub>y</sub> to Fe (N<sub>2</sub>) or Fe<sub>3</sub>O<sub>4</sub> (CO<sub>2</sub>). The mass gain (1.98%) observed only in N<sub>2</sub> that occurs slowly is attributed to the oxidation of Fe to FeO, and the oxidation occurs probably because the equipment is not hermetically sealed and/or a trace of oxygen in nitrogen and in carbon dioxide which were used as purge gas.

**Cobalt Compound.** The simultaneous TG – DTA curves in N<sub>2</sub> and CO<sub>2</sub> atmospheres are shown in Fig. 3c and c\*, respectively. The first mass loss between 110 – 225 °C (N<sub>2</sub>) or 110 – 235 °C (CO<sub>2</sub>), corresponding to the endothermic peak at 210 °C (N<sub>2</sub>) and 215 °C (CO<sub>2</sub>) is due to dehydration with loss of 2H<sub>2</sub>O (Calcd. = 18.29%, TG = 18.10% (N<sub>2</sub>), 18.37% (CO<sub>2</sub>)).

The thermal decomposition of the anhydrous compound occurs in two steps between 230 – 385 °C and 385 – 475 °C (N<sub>2</sub>) or 240 – 375 °C and 375 - 450 °C (CO<sub>2</sub>) with losses of 39.88% and 7.64% (N<sub>2</sub>) or 41.19% and 2.66% (CO<sub>2</sub>), respectively, corresponding to the endothermic peak at 340 °C (N<sub>2</sub>) and 335 °C (CO<sub>2</sub>) attributed to the pyrolysis of the compound with formation of a mixture of Co and CoO (N<sub>2</sub>) or CoO (CO<sub>2</sub>). The mass gain (3.32%) in N<sub>2</sub> atmosphere is attributed to the oxidation reaction of Co to CoO, as already observed in the iron compound.

The endothermic event between 675 – 820 °C with peak at 780 °C (CO<sub>2</sub>), is attributed to the slow pyrolysis of the carbonaceous residue. No mass loss is observed in the TG curve corresponding to this thermal event because the carbonaceous residue formed in this step is insufficient to sensitize the mass loss in the thermobalance. The presence of carbonaceous residue was confirmed with sample heated up to 600 °C in CO<sub>2</sub> atmosphere and the residue dissolved in nitric acid solution.

**Nickel Compound.** The simultaneous TG – DTA curves in N<sub>2</sub> and CO<sub>2</sub> atmospheres are shown in Fig. 3d and d\*, respectively. The first mass loss between 160 – 270 °C (N<sub>2</sub>) and 160 – 275 °C (CO<sub>2</sub>), corresponding to an endothermic peak at 250 °C (N<sub>2</sub>) and 260 °C (CO<sub>2</sub>) is due to dehydration with loss of 2H<sub>2</sub>O (Calcd. = 18.31%, TG = 18.51% (N<sub>2</sub>), 18.36% (CO<sub>2</sub>)).

After the dehydration the anhydrous compound shows mass losses in two steps up to 775 °C (N<sub>2</sub>) and 490 °C (CO<sub>2</sub>). The first step between 270 – 375 °C (N<sub>2</sub>) and 275 – 400 °C (CO<sub>2</sub>) corresponding to the endothermic peak

at 365 °C in both atmospheres, with loss of 49.24% (N<sub>2</sub>) and 50.07% is attributed to the pyrolysis of the compound with formation of a mixture of nickel oxide (Ni<sub>x</sub>O<sub>y</sub>) and carbonaceous residue. The last mass loss between 375 – 775 °C (N<sub>2</sub>) and 400 – 490 °C (CO<sub>2</sub>), corresponding to an endothermic event between 550 – 760 °C (N<sub>2</sub>) or an endothermic peak at 480 °C (CO<sub>2</sub>), with loss of 2.29% (N<sub>2</sub>) or 1.89%(CO<sub>2</sub>) is attributed to the pyrolysis of the carbonaceous residue and reduction reaction of Ni<sub>x</sub>O<sub>y</sub> to Ni. The mass gain (4%) between 600 and 1000 °C observed in the CO<sub>2</sub> atmosphere is attributed to the partial oxidation of Ni to NiO.

**Copper Compound.** The simultaneous TG – DTA curves in N<sub>2</sub> and CO<sub>2</sub> atmospheres are shown in Fig 3e and e\*, respectively. A great similarity is observed in the TG and DTA profiles in both atmospheres. The first mass loss between 60 and 160 °C, corresponding to an endothermic peak at 145 °C in both atmospheres is due to dehydration with loss of 2H<sub>2</sub>O (Calcd. = 17.87%, TG = 18.08% (N<sub>2</sub>), 17.80% (CO<sub>2</sub>)).

In both atmospheres, after the dehydration the thermal decomposition occurs in four steps and for the first three ones the mass loss begin through a slow process (160 – 240 °C), followed by a very fast one (240 – 250 °C) and fast process (250 – 315 °C), corresponding to a small endothermic peak at 250 °C with total loss of 46.85% (N<sub>2</sub>) and 46.45% (CO<sub>2</sub>) attributed to the pyrolysis of the compound with formation of a mixture of cuprous oxide and carbonaceous residue. The last mass loss between 315 – 880 °C (N<sub>2</sub>) and 315 – 710 °C (CO<sub>2</sub>) corresponding to an endothermic event between 650 – 900 °C (N<sub>2</sub>) and 550 – 720 °C (CO<sub>2</sub>) with loss of 4.15% (N<sub>2</sub>) and 4.73% (CO<sub>2</sub>) is attributed to the pyrolysis of carbonaceous residue and reduction reaction of Cu<sub>2</sub>O to Cu. The endothermic peak at 1070 °C (N<sub>2</sub>) is due to fusion of the copper.

**Zinc Compound.** The simultaneous TG – DTA curves in N<sub>2</sub> and CO<sub>2</sub> atmospheres are shown in Fig. 3f and f\*, respectively. The first mass loss between 100 – 190 °C (N<sub>2</sub>) or 100 – 200 °C (CO<sub>2</sub>), corresponding to an endothermic peak at 170 °C (N<sub>2</sub>) or 180 °C (CO<sub>2</sub>) is due to dehydration with loss of 2H<sub>2</sub>O (Calcd. = 17.71%, TG = 17.36% (N<sub>2</sub>), 17.43% (CO<sub>2</sub>)).

The anhydrous compounds is stable up to 235 °C (N<sub>2</sub>) or 240 °C (CO<sub>2</sub>) and above these temperatures the TG curve shows mass losses in two steps, although the DTA curve in N<sub>2</sub> atmosphere shows two overlapping steps for the first mass loss.

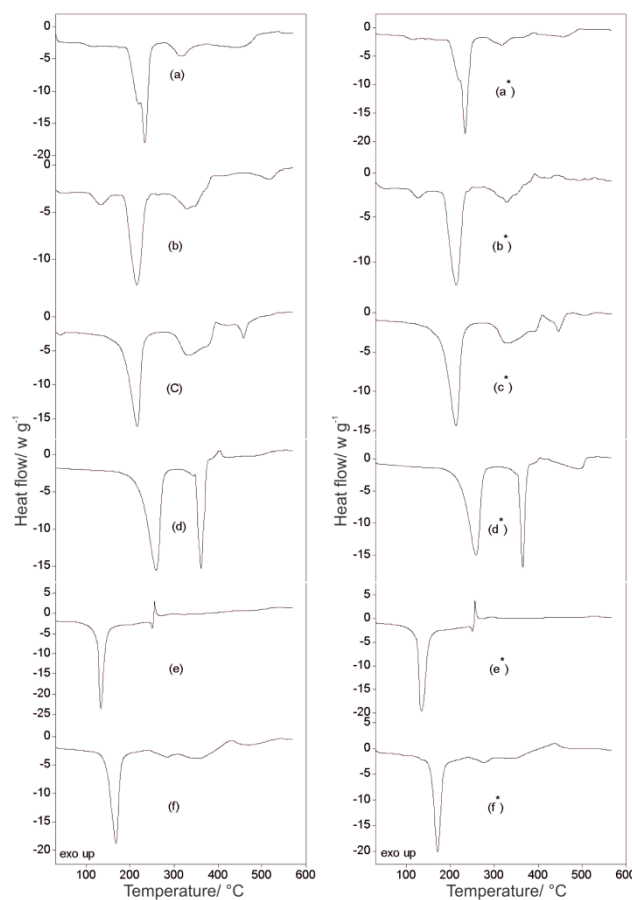
The mass loss between 235 – 430 °C (N<sub>2</sub>) and 240 – 445 °C (CO<sub>2</sub>), corresponding to endothermic peaks at 285 °C and 350 °C (N<sub>2</sub>) or 280 °C (CO<sub>2</sub>) with loss of 37.58% (N<sub>2</sub>) and 40.11% (CO<sub>2</sub>) is attributed to the pyrolysis of the compound with formation of a mixture of zinc oxide and carbonaceous residue. The last mass loss that occurs through a slow process, between 430 – 950 °C (N<sub>2</sub>) or 445 – 660 °C (CO<sub>2</sub>) corresponding to an endothermic event between 700 – 970 °C (N<sub>2</sub>) or 570 – 670 °C (CO<sub>2</sub>) with loss of 5.28% and 2.59%, respectively is attributed to the pyrolysis of the carbonaceous residue with formation of zinc oxide, ZnO, as final residue in both atmospheres.

For all the compounds the mass losses in each step of the TG curves, as well as the temperature where these losses

occur in both atmospheres are in disagreement with the results described in the literature [1]. It is well known that the experimental conditions affect the TG and DTA curves[8]. On that account the disagreements are observed.

### 3.3.2. DSC Curves

The DSC curves obtained in nitrogen and carbon dioxide atmospheres are shown in Fig. 4. These curves show endothermic peaks that are all in agreement with the thermal events observed in the DTA curves and exothermic peak for the nickel and copper compounds that is difficult to attribute in the DTA curves. Thus, the exothermic peak at 404 ° (Ni) and 256 °C (Cu) in both atmospheres, Fig. 4 (d, d\*) and (e, e\*), respectively, is attributed to the decarboxylation that occurs during the thermal decomposition.



**Figure 4.** DSC curves of the compounds in dynamic N<sub>2</sub> and CO<sub>2</sub>\* atmospheres: (a, a\*) MnL·2.5H<sub>2</sub>O (m = 2.041 mg; 2.082 mg\*), (b, b\*) FeL·2.5H<sub>2</sub>O (m = 2.049 mg; 2.088mg\*), (c, c\*) CoL·2H<sub>2</sub>O (m = 2.035 mg, 2.093 mg\*), (d, d\*) NiL·2H<sub>2</sub>O ( m = 2.060 mg, 2.028 mg\*), (e, e\*) CuL·2H<sub>2</sub>O (m = 2.057 mg; 2.147 mg\* ) and (f, f\*) ZnL·2H<sub>2</sub>O (m = 2.050 mg, 2.180 mg\*).

These curves also show that the profiles, as well as the temperature where the thermal event occurs, are in disagreement with those observed in the DTA curves. The disagreement is because the DSC and DTA curves were obtained in enough different conditions [8, 9]. The peaks temperatures (°C) observed in the DSC curves are shown in Table 1.

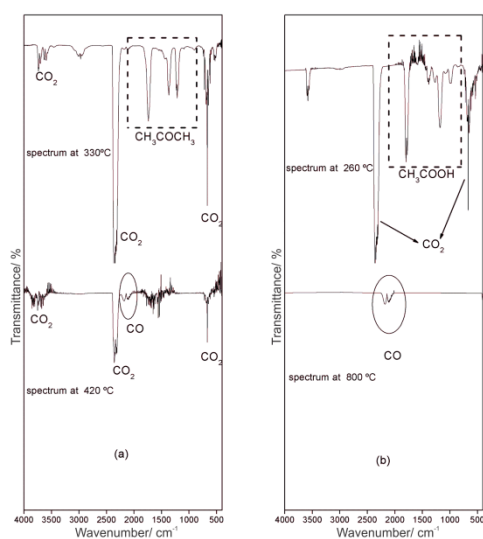
**Table 1.** Temperature (°C) of the peaks, endothermic\*, observed in the DSC curves of the compounds in N<sub>2</sub> and CO<sub>2</sub> atmospheres.

Compound	N <sub>2</sub>	CO <sub>2</sub>
C <sub>3</sub> H <sub>4</sub> O <sub>4</sub>	102, 136, 190	101, 136, 190
Na <sub>2</sub> C <sub>3</sub> H <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O	117, 328, 344, 367*	118, 328, 350, 369*
MnL·2.5H <sub>2</sub> O	114, 234, 317, 450	116, 234, 317, 363, 465
FeL·2.5H <sub>2</sub> O	134, 215, 329, 518	126, 214, 327
CoL·2H <sub>2</sub> O	216, 332, 458	213, 329, 446
NiL·2H <sub>2</sub> O	259, 361, 404*	259, 369, 405*, 494
CuL·2H <sub>2</sub> O	134, 250, 256*	135, 250, 257*, 296*
ZnL·2H <sub>2</sub> O	168, 284, 358, 475	171, 279, 350

L = malonate

### 3.3.3. Evolved gas analysis

The gaseous products evolved during the thermal decomposition of the sodium and transition metal ion compounds studied in this work were monitored by FTIR and identified on basis of their FTIR reference available on Nicolet libraries. The IR spectra of the gaseous products evolved during the thermal decomposition of copper and cobalt malonates, as representative of all the compounds, are shown in Fig. 5. For the sodium, manganese, iron, cobalt and zinc malonates, the volatile thermal decomposition products were identified as CO, CO<sub>2</sub> and acetone (a), while CO, CO<sub>2</sub> and acetic acid (b) were identified for the nickel and copper compounds.

**Figure 5.** IR spectra of gaseous products evolved during the decomposition of the compounds: (a) CoL·2H<sub>2</sub>O, (b) CuL·2H<sub>2</sub>O.

## 4. Conclusion

The present study showed that the thermal decomposition of malonic acid in dynamic N<sub>2</sub> and CO<sub>2</sub> atmospheres occurs with formation of acetic acid.

This study also showed that the gaseous products evolved during the thermal decomposition of Na, Mn, Fe, Co, and Zn compounds were: CO, CO<sub>2</sub> and acetone and for Ni and Cu compounds were: CO, CO<sub>2</sub> and acetic acid. The final residue of the thermal decomposition in nitrogen

atmosphere, up to 1100 °C was MnO, FeO, CoO, Ni, Cu and ZnO and in CO<sub>2</sub> atmosphere up to 1000 °C was Mn<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>, CoO, Ni + NiO, Cu and ZnO.

## Acknowledgements

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