

1 **Thermal analysis in oxidative and pyrolysis conditions of alkaline earth metals picolates using the**
2 **techniques: TG-DSC, DSC, MWTA, HSM and EGA (TG-DSC-FTIR and HSM-MS)**

3
4 A.L.C.S. Nascimento^{a,b}, G.M.B. Parkes^b, G.P. Ashton^b, R.P. Fernandes^a, J.A. Teixeira^a, W.D.G. Nunes^a,
5 M. Ionashiro^{a, 1}, F.J. Caires^{a,c}

6
7 *^a Instituto de Química, Universidade Estadual Paulista, CP 355, 14801-970 Araraquara, SP, Brazil*

8
9 *^b Thermal Methods Research Unit, Department of Chemistry, University of Huddersfield, Queensgate,*
10 *Huddersfield HD1 3DH, United Kingdom*

11
12 *^c Faculdade de Ciências, UNESP—Univ., Estadual Paulista, Campus Bauru, Departamento de*
13 *Química, Bauru, SP 17033-260, Brazil*

14
15 **ABSTRACT**

16 Synthesis, characterization, thermal stability and pyrolysis of some alkaline earth picolates
17 $M(C_6H_5NO_2)_2 \cdot nH_2O$ (where $M = Mg(II), Ca(II), Sr(II)$ and $Ba(II)$ and $n = di (Mg), mono (Ca), hemi three$
18 (Sr) hydrated) were investigated using a range of techniques including simultaneous thermogravimetry and
19 differential scanning calorimetry (TG–DSC), evolved gas analysis (EGA), differential scanning calorimetry
20 (DSC), Hot-Stage microscopy (HSM), powder X-ray diffractometry (PXRD), complexometry with EDTA
21 and elemental analysis (EA). The TG-DSC curves show that the hydrated compounds dehydrate in a single
22 step of mass loss and the thermal stability of the anhydrous compound is little influenced from the
23 atmosphere used. On the other hand, the mechanisms of thermal decomposition are profoundly influenced
24 by the atmosphere used, as can also be observed in the EGA data. In addition, a comparison between two
25 calorimetric techniques, Microwave Thermal Analysis (MWTA) and DSC, was made which showed similar
26 profiles. Two evolved gas analysis (EGA) techniques: TG-DSC coupled to FTIR and HSM coupled to a
27 quadrupole mass spectrometer (MS) were also used to provide additional information about the pyrolysis
28 mechanism.

29 **Keywords:** Alkaline earth picolates; Microwave Thermal Analysis (MWTA); TG-DSC-FTIR; HSM-
30 MS.

31 **1. INTRODUCTION**

32 2-Pyridinecarboxylic acid, also known as picolinic acid, has a six-membered ring structure with
33 two active groups: a carboxylic in the ortho-position to the nitrogen in the pyridine ring, therefore, the
34 potential donor sites leads to a variety of ligation modes [1]. Picolinic acid is a natural compound that

¹ **Corresponding author.**

e-mail address: massaoui@yahoo.com.br

35 exhibits chelating properties which facilitates the absorption of minerals such as: chromium, zinc,
36 magnesium, copper, iron, and probably molybdenum [2-3]. Picolinates have been reported to possess a
37 variety of therapeutic properties including neuroprotection, immunology, and anti-proliferative effects on
38 the body [4–8]. Selective complexation of metal ions is also an important requirement for the use of metal
39 complexes finding a range of applications within medicine. Indeed, chronic intoxication with a range of
40 metal ions can be treated with the administration of a suitable chelating agent [9-11].

41 The literature reports studies with picolinic N-oxide forming bivalent transition metals ions [12],
42 trivalent lanthanide ions [13–15], rare earth picolinate complexes [16-17] and others lanthanide complexes
43 [18]. Previous papers demonstrating the thermal behavior of lanthanides picolinates have been reported
44 [14,17], however, no systematic study about the thermal behavior of the alkaline earth metal picolinates has
45 been found.

46 Microwave heating is dependent on a parameter, $\tan \delta$, which is dependent on the dielectric
47 properties of the sample and is key to how well a material can convert electromagnetic energy into heat.
48 Microwave Thermal Analysis (MWTA) uses microwave energy as a means of simultaneously heating a
49 sample and detecting thermal transitions (phase changes, decomposition, etc.) through changes in the $\tan \delta$
50 of a sample. MWTA is most often used in a differential temperature configuration [19] where the difference
51 between the sample and an inert reference (SiC) is recorded. If a sample undergoes enthalpic changes but
52 no significant changes in $\tan \delta$ then the trace produced approximates that seen with a DTA/DSC. However,
53 if the sample undergoes a change that affects $\tan \delta$ this is shown as steps on the differential temperature
54 trace. For certain systems, MWTA has the potential for greater sensitivity than conventional DSC but this
55 is very sample dependent [20].

56 In recent years microwave heating has been used for processing and drying of chemicals
57 [21-23]. The suitability of the method for the drying of pharmaceuticals has been extensively investigated
58 [24], for example, with the application for maintenance of drug stability [25]. To date, MWTA has only
59 been applied to simple metal salts and hydrates and not more complex compounds such as picolinates.

60 The present paper aims to investigate the thermal behavior of picolinic acid and its compounds with
61 some alkaline earth ions: $\text{Mg}(\text{C}_6\text{H}_4\text{NO}_2)_2 \cdot 2\text{H}_2\text{O}$, $\text{Ca}(\text{C}_6\text{H}_4\text{NO}_2)_2 \cdot \text{H}_2\text{O}$, $\text{Sr}(\text{C}_6\text{H}_4\text{NO}_2)_2 \cdot 1.5\text{H}_2\text{O}$ and
62 $\text{Ba}(\text{C}_6\text{H}_4\text{NO}_2)_2$. The characterization was performed using thermoanalytical techniques
63 (TG-DSC, DSC, MWTA, and HSM) and complementary techniques such as PXRD. A comparison has
64 been made between hyphenated techniques to evaluate gaseous decomposition products of metal picolinates
65 through EGA using TG-DSC-FTIR and HSM-MS.

66

67 2. Experimental

68 2.1. Chemicals

69 Picolinic acid (99% purity) was obtained from Sigma and was used as received. The calcium,
70 strontium and barium carbonates were obtained from Fluka (Ca, 99.5%), Merck (Sr, Ba, 99% purity) and
71 magnesium carbonate was prepared as described in reference [28].

72

73 **2.2.Preparation**

74 Solid-state alkaline earth metal picolines (Mg to Ba) were synthesized following methodology
75 previously reported [28].

76

77 **2.3.Experimental equipment and conditions**

78 The composition of the compounds was determined by elemental analysis (CHN Elemental
79 Analyzer from Perkin Elmer, model 2400), TG data and EDTA complexometry [26, 27].

80 Simultaneous TG-DSC curves were obtained by using a TG-DSC 1 STAR^e system, from Mettler
81 Toledo and according to the methodology described in reference [14]. The purge gas used was either dry
82 air or nitrogen with a flow rate of 50 mL min⁻¹ and a heating rate of 10 °C min⁻¹, and samples weighing
83 approximately 10 mg in open alumina crucibles.

84 The DSC curves were obtained by using DSC STAR^e system, from Mettler Toledo. The purge gas
85 was nitrogen with a flow rate of 100 mL min⁻¹. A heating rate of 10 °C min⁻¹ was adopted, with samples
86 weighing about 3 mg placed in aluminum crucibles with a perforated lid.

87 The identification of evolved gases (EGA) in dynamic dry nitrogen atmosphere were carried out
88 using a TG-DSC 1 Mettler Toledo coupled to a Nicolet FTIR spectrophotometer with gas cell and DTGS
89 KBr detector using the method described in reference [29]. The furnace and heated gas cell (250 °C) were
90 coupled through a heated (225 °C) 120 cm stainless steel transfer line with diameter of 3.0 mm, both purged
91 with dry air and nitrogen (50 mL min⁻¹). The FTIR spectra were recorded with 16 scans per spectrum at a
92 resolution of 4 cm.

93 Hot-stage microscopy (HSM) measurements were performed using a system developed at
94 Huddersfield [30] which utilizes a stereoscopic microscope (Leica) and a water cooled hot-stage (HSM5,
95 Stanton-Redcroft). Samples were placed in 5-6 mm alumina crucibles using sample masses of 10 mg, linear
96 heating rates of 10 °C min⁻¹ under an inert atmosphere. Micrographs were recorded every 5 °C.

97 The HSM system was coupled to a quadrupole mass spectrometer (HPR20, Hiden, Warrington,
98 UK). Evolved sample gases were transferred via a heated capillary line to the inlet of the spectrometer, full
99 mass scans were recorded between 4 and 300 mass units with an accumulation time of 200 ms per scan.

100 Microwave thermal analysis was performed using an instrument previously developed at
101 Huddersfield [19]. The system utilizes a 300 W 2.45 GHz generator (Sairem) and a single mode waveguide.
102 The generator is computer controlled with a power resolution corresponding to 1W. The standing wave is

103 tuned to achieve the maximum of the E-field over the position of the sample. Samples of 40 mg were placed
104 within silica crucibles (fundamentally microwave transparent) and heated at a rate of 10 °C min⁻¹ up to an
105 upper temperature of 450 °C. DTA microwave measurements are made between the sample and a reference
106 of silicon carbide.

107 Powder X-Ray Diffraction (PXRD) patterns analyses were obtained using a Bruker D2 Phaser
108 employing CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) and settings of 30 KV and 10 mA. The analysis were performed
109 in an angular range from 5 - 80 ° (2 θ), scanning speed 0.5 seconds, and 0.02° steps.

110

111 **3. Results and discussions**

112 **3.1. Analytical results**

113 The analytical results (TG, EA and EDTA complexometry) of the synthesized compounds are
114 shown in Table 1. These results are in close agreement with each other and with the calculated theoretical
115 values, which shows that the compounds were obtained with excellent purity. In addition, from these results
116 it was possible to determine the empirical formula of these compounds, which is in agreement with the
117 general formula: M(L)₂nH₂O, where M represents Mg, Ca, Sr and Ba, L is picolinate and n = 2 (Mg), 1
118 (Ca), 1.5 (Sr) and 0 (Ba).

119

119 **Insert Table 1**

120

121 **3.2. Thermal Analysis**

122 The simultaneous enthalpy and mass loss curves from TG-DSC curves in dynamic dry air and
123 nitrogen atmospheres are shown in Fig.1 (a-d) and (a*-d*), respectively. In an air atmosphere, these curves
124 exhibit mass losses in either a single (Ba), three (Mg, Sr) or four (Ca) steps. While for nitrogen three (Mg,
125 Sr, Ba) and four (Ca) steps were observed.

126 Thermal decomposition of the picolinate compounds in an oxidative atmosphere was monitored up
127 to 1000°C, the final residues for Mg, Ca and Sr were the respective oxides and carbonate for barium. In
128 contrast, the pyrolytic atmosphere (N₂) shows gradual mass losses that are still apparent up to 1000 °C for
129 Mg, Sr and Ba (forming a mixture of respective oxides and charred material) with only Ca picolinate
130 forming its oxide within this temperature range.

131 The TG-DSC profiles of the compounds in air atmosphere are not the same in N₂, thus these curves
132 in each atmosphere are discussed separately below.

133 The DSC and MWTA provided information necessary for identification of the physical phenomena
134 of melting (Mg, Ca), glass transitions (Mg, Ca), and phase transitions (Ba, Ca). The dehydration of all the
135 compounds, except barium, is more clearly observed using DSC rather than simultaneous TG-DSC data.

136

137

138 3.2.1. TG-DSC under an air atmosphere

139 The simultaneous TG-DSC curves of the compounds in an air atmosphere are shown in Fig. 1
140 (a-d). The TG curve shows that the barium compound was obtained as anhydrous, while calcium compound
141 as mono-hydrate, strontium and magnesium as hemi-three and di-hydrated, respectively. These curves also
142 show that the dehydration in all the compounds (except barium) occurs in a single step. The thermal stability
143 of the hydrated compounds, as well as the final temperature of thermal decomposition to the respective
144 oxides as shown by TG-DSC curves, depends on the nature of the metal ion and follow the order:

145 Dehydration stability: $Mg > Ca > Sr$

146 Decomposition stability: $Ba > Sr > Ca = Mg$

147 The thermal behavior of the compounds is also dependent on the nature of the metal ion and so the
148 features of each of these compounds are discussed individually.

149 Magnesium picolinate

150 The simultaneous TG-DSC curves are shown in Fig.1 (a). The first mass loss between 50 and 175
151 °C, with a corresponding endothermic peak at 148 °C is attributed to the dehydration with loss of
152 2 H₂O ($\Delta m_{calc.} = 11.76\%$, $\Delta m_{TG} = 12.27\%$). The anhydrous compound is stable up to 390 °C. Above this
153 temperature the mass losses occurs in two overlapping steps between 390-415 °C ($\Delta m_{TG} = 35.07\%$) and
154 415-550 °C ($\Delta m_{TG} = 39.26\%$), corresponding to an endothermic peak at 408 °C and is attributed to the
155 beginning of thermal decomposition. An exothermic peak at 490 °C, with shoulder at 460 °C is attributed
156 to the thermal decomposition and oxidation of the organic matter and/or the gaseous products evolved
157 during the thermal decomposition, respectively. The total mass loss up to 535 °C is in agreement with the
158 formation of magnesium oxide (MgO), as the final residue ($\Delta m_{calc.} = 86.61\%$, $\Delta m_{TG} = 86.85\%$).

159 The small endothermic peak at 398 °C, at the beginning of the mass loss is due to the melting of
160 the compound as discussed in the DSC and MWTA sections.

161

162 Calcium picolinate

163 The simultaneous TG-DSC curves are shown in Fig 1 (b). The first mass loss up to 170 °C,
164 corresponding to an endothermic peak at 145 °C and is attributed to the dehydration with loss of H₂O ($\Delta m_{calc.}$
165 $= 5.92\%$, $\Delta m_{TG} = 6.23\%$).

166 The anhydrous compound is stable up to 390 °C and above this temperature the thermal
167 decomposition occurs in three consecutive steps, with the first two overlapping. The two overlapping mass
168 loss steps observed between 390-460 °C ($\Delta m_{TG} = 35.89\%$) and 460-515 °C ($\Delta m_{TG} = 23.95\%$) have an

169 exothermic peak centred at 460 °C. These changes are attributed to oxidation of the organic matter and/or
170 the loss of gaseous products evolved during the thermal decomposition. The total mass loss up to 515 °C is
171 in agreement with the formation of calcium carbonate as a residue ($\Delta m_{\text{calc.}} = 66.89\%$, $\Delta m_{\text{TG}} = 66.91\%$)
172 which is stable until about 570 °C.

173 The final mass loss step observed between 570 °C and 700 °C ($\Delta m_{\text{TG}} = 14.75\%$), is attributed to the
174 thermal decomposition of the carbonate to the calcium oxide as a final residue ($\Delta m_{\text{calc.}} = 14.56\%$, $\Delta m_{\text{TG}} =$
175 14.43%). The total mass loss up to 670 °C is in agreement with the formation of calcium oxide, CaO, as
176 final residue (Calcd. = 81.59%, TG = 81.55%).

177 The very small exothermic peak at 275 °C and the endothermic peak at 360 °C (both not associated
178 with a mass loss from the TG curve) are attributed to crystallization process and melting of the compound.
179 These processes were more apparent HSM, DSC and MWTA as discussed latter.

180

181 Strontium picolinate

182 The simultaneous TG-DSC curves are shown in Fig. 1 (c). A gradual mass loss is observed up to
183 300 °C, although no events on the DSC curve are apparent. To evaluate this mass loss, the sample was
184 heated in a glass tube up to 300 °C for 15 min where evaporation followed by condensation was observed.
185 The residue condensed on the wall of the tube was analyzed using FTIR which confirmed that water was
186 evolved. Therefore the gradual mass loss was attributed to dehydration with loss of 1.5H₂O ($\Delta m_{\text{calc.}} =$
187 7.49% , $\Delta m_{\text{TG}} = 7.11\%$).

188 The anhydrous compound remained stable up to 415 °C but above this temperature mass loss occurs
189 through a fast process corresponding to a large and sharp exothermic peak at 450 °C. This mass change is
190 attributed to thermal decomposition and oxidation of the organic matter. The mass loss up to 500 °C is in
191 agreement with the formation of strontium carbonate as residue ($\Delta m_{\text{calc.}} = 55.51\%$, $\Delta m_{\text{TG}} = 55.43\%$), which
192 is stable up to 790 °C.

193 The last mass loss occurs between 790 °C and 940 °C is attributed to the thermal decomposition of
194 the carbonate to the strontium oxide SrO, as final residue ($\Delta m_{\text{calc.}} = 11.40\%$, $\Delta m_{\text{TG}} = 12.04\%$).

195 Barium picolinate

196 The simultaneous TG-DSC curves are shown in Fig 1 (d). The anhydrous compound is stable up
197 to 400 °C and above this temperature the thermal decomposition occurs through a fast process
198 corresponding to a large and a sharp exothermic peak at 475 °C with shoulder at 440 °C. These changes are
199 attributed to oxidation of the organic matter and/or the loss of gaseous products evolved during the thermal
200 decomposition. The mass loss up to 500 °C is in agreement with the formation of barium carbonate as

201 residue ($\Delta m_{\text{calc.}} = 50.27\%$, $\Delta m_{\text{TG}} = 50.66\%$). The barium carbonate, BaCO_3 , formed is stable to 920 °C but
202 above this temperature begins further decomposition which has not completed by 1000 °C.

203 The very small endothermic peaks at 211 °C and 780 °C, (both not associated with a mass loss from
204 the TG curve) , have been tentatively assigned to crystalline phase transition (corresponding to the
205 endothermic peak on DSC curve at 241 °C, see in Figure 4) and phase transformation (α - β) of the barium
206 carbonate, respectively.

207 **Insert Figure 1**

208 3.2.2. TG-DSC – N_2 atmosphere

209 The simultaneous TG and DSC curves of the compounds are shown in Fig. 1 (a*-d*). These curves
210 show mass losses in consecutive steps and endothermic peaks corresponding to the losses or due to physical
211 phenomenon.

212 The thermal stability of the hydrated and anhydrous compounds depends on the nature of the metal
213 ion and they follow the order:

214 Dehydration stability: $\text{Ca} > \text{Mg} > \text{Sr}$

215 Decomposition stability: $\text{Ba} > \text{Sr} > \text{Ca} = \text{Mg}$

216 For all hydrated compounds, the dehydration step is, as expected, very similar to that observed in
217 the oxidizing atmosphere. However, a significant difference is observed in the thermal decomposition of
218 these compounds, suggesting a strong influence of the atmosphere. The final temperature of the thermal
219 decomposition is observed only for the calcium compound, for the other compounds the mass loss is
220 incomplete by 1000 °C.

221 As previously observed in an air atmosphere, and as will be shown for a N_2 one, the thermal
222 behavior also depends on the nature of the metal ion, features of each of these compounds are discussed
223 individually.

224 Magnesium picolinate

225 The simultaneous TG-DSC curves are shown in Fig. 1 (a*). The first step between 50 °C and 170
226 °C, corresponding to an endothermic peak at 165 °C is attributed to dehydration with loss of $2\text{H}_2\text{O}$ in the
227 same way as the oxidative atmosphere ($\Delta m_{\text{calc.}} = 11.83\%$, $\Delta m_{\text{TG}} = 11.42\%$). The anhydrous compound is
228 stable up to 385 °C and above this temperature the thermal decomposition occurs in two consecutive steps,
229 a sharp step between 385-490 °C ($\Delta m_{\text{TG}} = 42.34\%$) and a slow mass loss starting 490 °C ($\Delta m_{\text{TG}} = 27.78\%$)
230 which correspond to small, broad endothermic peaks at 450 °C and 950 °C. These steps have been attributed
231 to the thermal decomposition and incomplete pyrolysis of the compound. The endothermic peak at 390 °C
232 has been attributed to the melting of the magnesium compound.

233 Calcium picolinate

234 The simultaneous TG-DSC curves are shown in Fig. 1 (b*). The first mass loss with a
235 corresponding endothermic peak at 175 °C is attributed to the dehydration which, again, shows similarities
236 to the air example ($\Delta m_{\text{calc.}} = 5.96\%$, $\Delta m_{\text{TG}} = 5.83\%$).

237 The anhydrous compound remains stable up to 390 °C and above this temperature the thermal
238 decomposition occurs in three consecutive steps between 390-520 °C ($\Delta m_{\text{TG}} = 46.68\%$), 520-740 °C (Δm_{TG}
239 $= 20.57\%$) and 740-920 °C ($\Delta m_{\text{TG}} = 9.40\%$), corresponding to endothermic peaks at 415 °C, 425 °C, 435
240 °C, 730 °C and 845 °C, the first step is attributed to the thermal decomposition of the compound with
241 formation of calcium carbonate and carbonized residue and the last two steps to the pyrolysis of the
242 carbonized residue and thermal decomposition of calcium carbonate leading to calcium oxide ($\Delta m_{\text{calc.}} =$
243 81.45% , $\Delta m_{\text{TG}} = 81.48\%$).

244 The minor exothermic peak at 305 °C and the endothermic peak at 390 °C, (both not associated
245 with a mass loss from the TG curve) are attributed to crystallization process and fusion of the compound,
246 respectively.

247

248 Strontium picolinate

249 The simultaneous TG-DSC curves are shown in Fig. 1 (c*). A small broad mass loss is noted
250 between 50 and 300 °C which has been attributed to dehydration with loss of 1.5H₂O ($\Delta m_{\text{calc.}} = 7.49\%$,
251 $\Delta m_{\text{TG}} = 7.08\%$). The anhydrous compound is stable up to 420 °C but above this temperature, the mass losses
252 occur in three consecutive steps, between 420-550 °C ($\Delta m_{\text{TG}} = 36.33\%$), 550-800 °C ($\Delta m_{\text{TG}} = 25.16\%$) and
253 800-1000 °C ($\Delta m_{\text{TG}} = 7.17\%$). The first mass loss is attributed to thermal decomposition and the second
254 one to the pyrolysis of the strontium carbonate formed and/or charred residue. However, there is some
255 indication that the final mass loss is incomplete by 1000 °C.

256

257 Barium picolinate

258 The simultaneous TG-DSC curves are shown in Fig. 1 (d*). The anhydrous compound is stable up
259 to 450 °C but above this temperature the mass losses occur in three consecutive steps between 450-530 °C
260 ($\Delta m_{\text{TG}} = 27.66\%$), 530-800 °C ($\Delta m_{\text{TG}} = 19.73\%$) and 800-1000 °C ($\Delta m_{\text{TG}} = 10.32\%$). The first mass loss
261 (with an associated endotherm at 490 °C) is attributed to thermal decomposition to barium carbonate and
262 organic residue. This occurs at a much lower temperature under nitrogen due to the absence of CO₂
263 in this atmosphere as was previously reported [28]. The second broad mass loss step (with an associated

264 endotherm at 750 °C) is attributed to pyrolysis of the residue. However, there is some indication of further
265 mass loss which is incomplete by 1000 °C.

266 The endothermic peak at 245 °C without mass loss is due to the crystalline transition of the
267 compound (see in section 3.3, discussion about Figure 5).

268

269 3.3. Differential Scanning Calorimetry (DSC)

270 The DSC curves under a nitrogen atmosphere are shown in Figs. 2 to 5 together with associated
271 HSM and PXRD data to aid the visualization of the phenomenon attributed to physical or chemical
272 processes. This combination of data sets has provided information that expands on what the TG-DSC curves
273 have already shown, but has helped elucidate unresolved thermal events.

274 Figure 2 shows the DSC curve for the magnesium picolinate with three thermal events attributed
275 to dehydration (endothermic peak at 200 °C), melt (endothermic peak at 391 °C), where the enthalpies found
276 for the compound were -0.453 kJ g^{-1} and -0.002 kJ g^{-1} , respectively, and glass transition (midpoint at 254
277 °C). PXRD analysis shows that the structure varies with heating (see insert 1 diffractogram at 25 °C and
278 insert 2, diffractogram at 270 °C) are significantly different from each other as above the glass transition
279 temperature the compound becomes amorphous. Changes in the color of the compound were observed after
280 the glass transition and also at the start of melt at 370 °C. The slight darkening of the sample above 370 °C
281 is attributed to be the onset of decomposition.

282 **Insert Figure 2**

283

284 Figure 3 (a) shows the DSC curve with four thermal events attributed to dehydration (endothermic
285 peak at 188 °C), phase transition (peak at 303 °C), melt (peak at 388 °C), where the enthalpies found for the
286 compound were -0.254 kJ g^{-1} , $+0.055 \text{ kJ g}^{-1}$ and -0.096 kJ g^{-1} respectively, and a possible glass transition
287 (midpoint at 246 °C). The three PXRD patterns (1, 2 and 3) show a reduction in Bragg peaks as the
288 temperature is increased attributed to the loss of crystallinity. The thermally cycled DSC experiment (Figure
289 3 (b)) shows that the thermal event at 303 °C is irreversible. The micrographs show that the sample contracts
290 between 240 °C and 275 °C which may be due to a glass transition. The final micrograph at 390 °C clearly
291 shows the effect of melting.

292 **Insert Figure 3**

293 Figure 4 (a) show the DSC curve for strontium picolinate which is poorly resolved at the heating
294 rate used. Figure 4 (b) show the cycled DSC curve using a slow heating rate (2 °C min^{-1}) to increase
295 resolution. An endothermic event with peak at 176 °C was observed where the dehydration enthalpy found
296 was -0.332 kJ g^{-1} . Neither DSC curves clearly show other thermal events. However, for confirmation, the

297 sample was analyzed using PXRD before and after dehydration. The PXRD patterns indicate that the
298 compound increases in crystallinity after dehydration. Large changes in the color of the compound are
299 shown in the HSM micrographs before and after dehydration and, unlike the other picolinate, the strontium
300 compound starts to degrade without showing signs of melting.

301 **Insert Figure 4**

302 Figure 5 (a) shows the DSC curve for barium picolinate with two thermal events attributed to phase
303 transformation (endothermic peak at 113 °C) and crystalline transition (endothermic peak at 241 °C), the
304 enthalpies found were $-0,003 \text{ kJ g}^{-1}$ and $-0,016 \text{ kJ g}^{-1}$, respectively. For this compound, the DSC analysis
305 was very important since phase transformation cannot be observed directly using TG-DSC curves in both
306 atmospheres. The source of the sharp endothermic peak at 241 °C is unassigned. Although very similar to
307 what would be observed for melting, the HSM clearly shows that this does not occur. The cycle DSC
308 experiment (Fig. 5b) show that the endothermic peaks at 113 °C and 241 °C are both reversible so it was
309 not possible to obtain material for PXRD analysis.

311 **Insert Figure 5**

313 3.4. Microwave Thermal Analysis (MWTA)

314 Figure 6 (a-d) displays differential temperature traces obtained using MWTA for the four picolinate
315 compounds. It should be noted that the relatively large drift in the baseline is not uncommon for this
316 technique.

317 Figure 6 (a) shows the MWTA trace for magnesium picolinate. The first noticeable transition is an
318 endothermic peak around 200 °C attributed to the dehydration of the compound as also observed with DSC.
319 Further heating yields a slight increase in coupling with microwave energy possibly linked to the glass
320 transition shown in the DSC curve. The the onset of decomposition, as confirmed by TG-DSC curve, is
321 apparent from the variation in the baseline followed by a sharp step above 400 °C. Upon cooling two main
322 steps are seen, but are difficult to assign because full decomposition was not achieved.

323 **Insert Figure 6**

324
325 Figure 6 (b) show the MWTA trace for calcium picolinate. The endothermic dehydration can be
326 seen at 200 °C and is clearly observed mirroring the signal obtained by the DSC. No indication of a glass
327 transition was observed, although the attributed crystalline phase change at 300 °C shows a corresponding

328 step change in $\tan \delta$. The melting/decomposition step at 380 °C is at a similar temperature to that noted on
329 the DSC, since the calcium picolinate exists in a liquid state now the sample can be seen to couple more
330 strongly with the microwave energy.

331 The MWTA trace for strontium picolinate is shown in Figure 6 (c). Unlike the DSC, the MWTA
332 has few features and no discernible sign of dehydration. There is a suggestion of a change at 413 °C that
333 could be associated with decomposition onset although this process unlikely reached completion by 450
334 °C.

335 The MWTA trace for barium picolinate is shown in Figure 6 (d). The small step change at 250 °C
336 has been attributed to the crystalline phase change observed using DSC. The baseline does not vary
337 significantly after this event and no significant events are seen during cooling.

338 3.5. Evolved Gas Analysis (EGA) of magnesium picolinate

339 Initial experiments using TG-DSC-FTIR showed all the four picolates studied yielded water, carbon
340 monoxide, carbon dioxide and pyridine (except water for barium compound which is anhydrous). The
341 decomposition of magnesium picolinate was probed in more detail using HSM-MS. Figure 7 shows the IR
342 spectra of the gaseous products evolved during the thermal decomposition of magnesium picolinate at 10
343 °C min⁻¹. Figure 7 (a) shows the Gram-Schmidt trace which gives an indication of the FTIR intensity over
344 time with three steps evident that can be linked to the TG-DSC curves in Figure 1(a*). Figure 7 (b) shows
345 the FTIR spectra at 160 °C (Step1) 430 °C (Step 2). The first spectra clearly shows the water produced
346 during dehydration while the second spectra confirms that pyridine is produced during decomposition.

347 **Insert Figure 7**

348
349 Figure 8 shows the decomposition of magnesium picolinate monitored using HSM-MS with an inert
350 atmosphere. Three gaseous compounds are plotted water (18 Da), carbon dioxide (44 Da) and pyridine (79
351 Da). The pyridine was confirmed by monitoring of the pyridine fragment ions (26, 27, 39 and 52 Da) but
352 these have not been shown for clarity. The results confirm those observed with TG-DSC-FTIR with water
353 being the sole product during the dehydration and pyridine being apparent during the decomposition stage.
354 The HSM-MS indicates that both water and carbon dioxide are released during the decomposition
355 indicating that the process is more complex than suggested by FTIR.

356 **Insert Figure 8**

357
358

359 4. CONCLUSIONS

360 From the elemental analysis, complexometry and thermogravimetric results the stoichiometry of
361 the compounds were determined as the having the empirical formula: $M(L)_2.nH_2O$.

362 The TG–DSC results provided previously unreported information about the thermal stability and
363 thermal decomposition of these compounds under oxidative and inert atmospheres. These results show that
364 the atmosphere used plays a significant role in the thermal decomposition process of this class of
365 compounds, since thermal stability, thermoanalytical curves and mass loss steps are all affected.

366 TG-DSC-FTIR analysis of the gaseous products from magnesium picolinate demonstrates that the
367 main decomposition proceeds with release of pyridine, CO and CO₂. The ability of HSM-MS to monitor
368 multiple ions confirms the evolution of pyridine and suggests that thermal degradation occurs by a much
369 more complex mechanism than suggested by TG-DSC-FTIR.

370 The DSC and MWTA data provided information about the physical transformation undergone by
371 the picolinate. For these compounds the decomposition did not appear to lead to significant changes in \tan
372 δ and thus MWTA was less sensitive than DSC.

373 The results further demonstrate the use of powder X-ray diffractometry in the elucidation of thermal
374 processes.

375

376 5. ACKNOWLEDGMENTS

377 The authors thanks University of Huddersfield, FAPESP (Proc. 2017/14936-9 and 2018/12463-9), CNPq
378 (Proc. 421469/2016-1) and CAPES Foundations (Brazil) for financial support. This research was supported
379 by resources supplied by PDSE from CAPES Foundation (Proc. 88881.135291/2016-01).

380 6. REFERENCES

381 [1] SOMPHON, W.; HALLER, K. J. Crystal growth and physical characterization of picolinic acid
382 cocrystallized with dicarboxylic acids. **Journal of Crystal Growth**, v. 362, n. 1, p. 252–258, 2013.

383 [2] SUZUKI, K.; YASUDA, M.; YAMASAKI, K. Stability constants of picolinic and quinaldic acid
384 chelates of bivalent metals. **Journal of Physical Chemistry**, v. 61, n. 2, p. 229–231, 1957.

385 [3] REBELLO, T.; LONNERDAL, B.; HURLEY, L. S. Picolinic acid in milk, pancreatic juice, and
386 intestine: inadequate for role in zinc absorption. **American Journal of Clinical Nutrition**, v. 35, n. 1, p.
387 1–5, 1982.

388 [4] WANG, X.; DAVIS, I. *et al.* Improved separation and detection of picolinic acid and quinolinic acid by
389 capillary electrophoresis-mass spectrometry: Application to analysis of human cerebrospinal fluid. **Journal**
390 **of Chromatography A**, v. 1316, p. 147–153, 2013.

391 [5] SHARMA, G.; NARULA, A. K. Synthesis and optoelectronic properties of three Eu(III)-dipicolinate
392 complexes based on α -picolinic acid, 2-aminopyridine and 2-hydroxypyridine as secondary ligands.

- 393 **Journal of Materials Science: Materials in Electronics**, v. 26, n. 2, p. 1009–1017, 2014.
- 394 [6] CHUANG, S. C.; FANIDI, A. *et al.* Circulating biomarkers of tryptophan and the kynurenine pathway
395 and lung cancer risk. **Cancer Epidemiology Biomarkers and Prevention**, v. 23, n. 3, p. 461–468, 2014.
- 396 [7] YUOH, A. C. B.; AGWARA, M. O. *et al.* Synthesis, Crystal Structure and Antimicrobial Properties of
397 an Anhydrous Copper(II) Complex of Pyridine-2-Carboxylic Acid. **International Journal of Chemistry**,
398 v. 7, n. 1, p. 10–20, 2014.
- 399 [8] LI, D.; ZHONG, G. Synthesis, Crystal Structure, and Thermal Decomposition of the Cobalt (II)
400 Complex with 2-Picolinic Acid. **The Scientific World Journal**, v. 2014, p. 1-7, 2014.
- 401 [9] MACKAY, D.; HATHCOCK, J.; GUARNERI, E. Niacin: chemical forms, bioavailability, and health
402 effects. **Nutrition Reviews**, v. 70, n. 6, p. 357–366, 2012.
- 403 [10] REGUEIRO-FIGUEROA, M.; RUSCSÁK, E. *et al.* Highly Stable Complexes of Divalent Metal Ions
404 (Mg^{2+} , Ca^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+}) with a DOTA-Like Ligand Containing a Picolinate Pendant.
405 **European Journal of Inorganic Chemistry**, v. 2014, n. 36, p. 6165–6173, 2014.
- 406 [11] CARLESON, L. A. Nicotinic acid: the broad-spectrum lipid drug. A 50th anniversary review, **Journal**
407 **of Internal Medicine**, v. 258, n. 2, p. 94–114, 2005.
- 408 [12] BOYD, S. A.; KOHRMAN, R. E.; WEST, D. X. Transition metal ion complexes of 2-picolinate N-
409 oxide. **Journal of Inorganic and Nuclear Chemistry**, v. 38, n. 3, p. 607–608, 1976.
- 410 [13] BOYD, S. A.; KOHRMAN, R. E.; WEST, D. X. Cationic lanthanide complexes of 2-picolinic acid n-
411 oxide. **Inorganic Nuclear Chemistry Letters**, v. 12, n. 8, p. 603–608, 1976.
- 412 [14] DO NASCIMENTO, A. L. C. S.; TEIXEIRA, J. A. *et al.* Thermal behavior, spectroscopic study and
413 evolved gas analysis (EGA) during pyrolysis of picolinic acid, sodium picolinate and its light trivalent
414 lanthanide complexes in solid state. **Journal of Analytical and Applied Pyrolysis**, v. 119, p. 242-250,
415 2016.
- 416 [15] LIS, S.; PISKUŁA, Z.; KUBICKI, M. The structure and spectroscopy of lanthanide(III) complexes
417 with picolinic acid N-oxide in solution and in the solid state. **Materials Chemistry and Physics**, v. 114, n.
418 1, p. 134–138, 2009.
- 419 [16] KECK, N. B.; HORNUNG, N. J.; BOS, W. G. The preparation and characterization of some rare earth
420 picolinate complexes. **Journal of Inorganic and Nuclear Chemistry**, v. 36, n. 7, p. 1521–1525, 1974.
- 421 [17] MOYNE, L.; THOMAS, G. Etude thermogravimétrique des picolates et dipicolates de lanthane,
422 praséodyme et néodyme. **Analytica chimica acta**, v. 29, p. 66–69, 1963.
- 423 [18] GOMES, D. J. C.; CAIRES, F. J. *et al.* Synthesis, characterization, thermal and spectroscopic studies
424 of solid glycolate of light trivalent lanthanides, except promethium. **Thermochimica Acta**, v. 587, p. 33–
425 41, 2014.
- 426 [19] Parkes, G. M. B.; Barnes, P.A. *et al.* Microwave thermal analysis - A new approach to the study of the
427 thermal and dielectric properties of materials. **Journal of Thermal Analysis and Calorimetry**, v. 56, p.
428 723-731, 1999
- 429
- 430 [20] Parkes, G. M. B.; Barnes, P.A. *et al.* Development of a new instrument for performing microwave
431 thermal analysis. **Review of Scientific Instruments**, v. 71, p. 168, 2000
- 432
- 433 [21] NMAB-473 Publication, Committee on microwave processing of materials: an emerging industrial
434 technology. Microwave processing of materials. Washington DC, USA: National Academy Press;1994.

- 435
436 [22] KINGSTON, H. M.; HASWELL S. J. Microwave enhanced chemistry. Washington, USA:
437 American Chemical Society; 1997.
438
- 439 [23] CHEE S, N.; JOHANSEN, A. L. *et al.* Microwave drying of granules containing a moisture sensitive
440 drug: a promising alternative to fluid bed and hot air oven drying. **Chemical and Pharmaceutical Bulletin**,
441 v. 53, n. 7, p. 770-775, 2005.
442
- 443 [24] LOH, Z. H.; LIEW, C. V. *et al.* Microwave-assisted drying of pharmaceutical granules and its impact
444 on drug stability. **International Journal of Pharmaceutics**, v. 359, n. 1-2, p.53-62, 2008.
445
- 446 [25] MONEGHINI, M.; ZINGONE G.; DE ZORDI, N. Influence of the microwave technology on the
447 physical–chemical properties of solid dispersion with nimesulide. **Powder Technology**, v. 195, n. 3, p.
448 259-63, 2009.
449
- 450 [26] FLASCHKA, H. A. EDTA Titrations and Introduction to Theory and Practice, 2nd ed., Press Oxford,
451 Pergamon, 1964.
- 452 [27] IONASHIRO, M.; GRAMER, C. A. F.; ZUANON NETTO, J. Titulação complexométrica de
453 lantanídeos e ítrio. **Eclética Química**, v. 8, n. 1, p. 29-32, 1983.
- 454 [28] NASCIMENTO, A. L. C. S.; CAIRES, F. J. *et al.* Thermal study and characterization of nicotines
455 of some alkaline earth metals using TG–DSC–FTIR and DSC-system photovisual. **Thermochimica Acta**,
456 v. 604, p. 7-15, 2015.
- 457 [29] TEIXEIRA, J. A.; NUNES, W. D. G. *et. al.* Thermal behavior in oxidative and pyrolysis conditions
458 and characterization of some metal p-aminobenzoate compounds using TG–DTA, EGA and DSC-
459 photovisual system. **Journal of Analytical and Applied Pyrolysis**, v. 128, p. 261-267, 2017.
- 460 [30] Berger, B.; Brammer, A. J. *et al.* Thermomicroscopy studies on the zirconium-potassium perchlorate-
461 nitrocellulose pyrotechnic system. **Thermochimica Acta**. v. 269/270, p. 639-648, 1995.

462

463

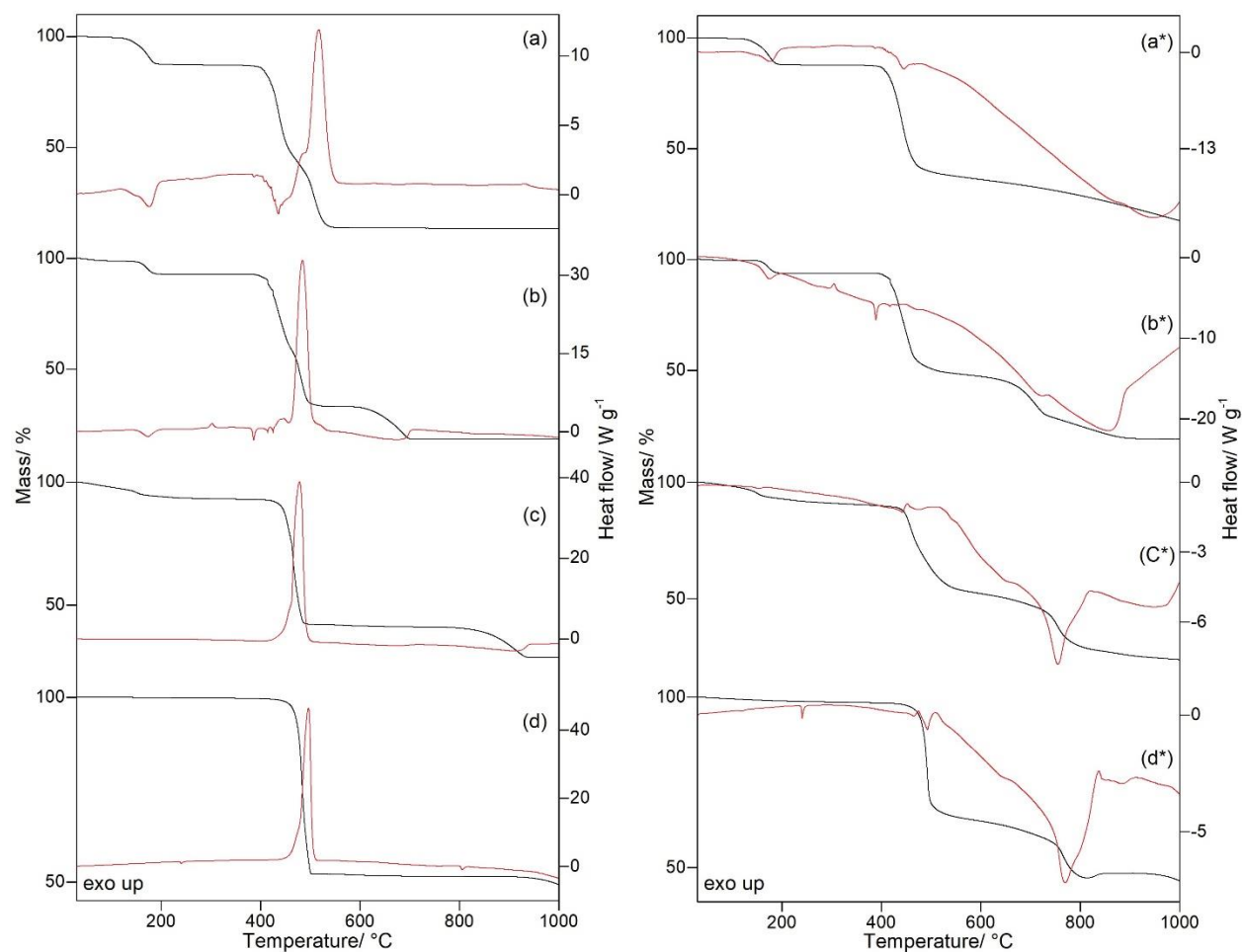
464

465

466

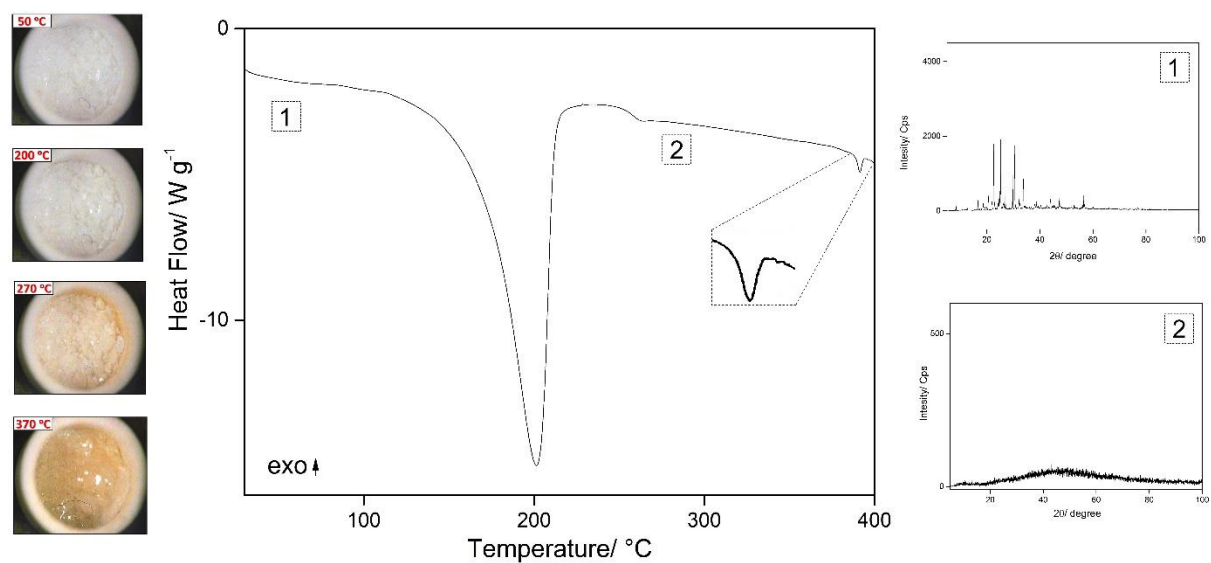
467

468 **Figures**



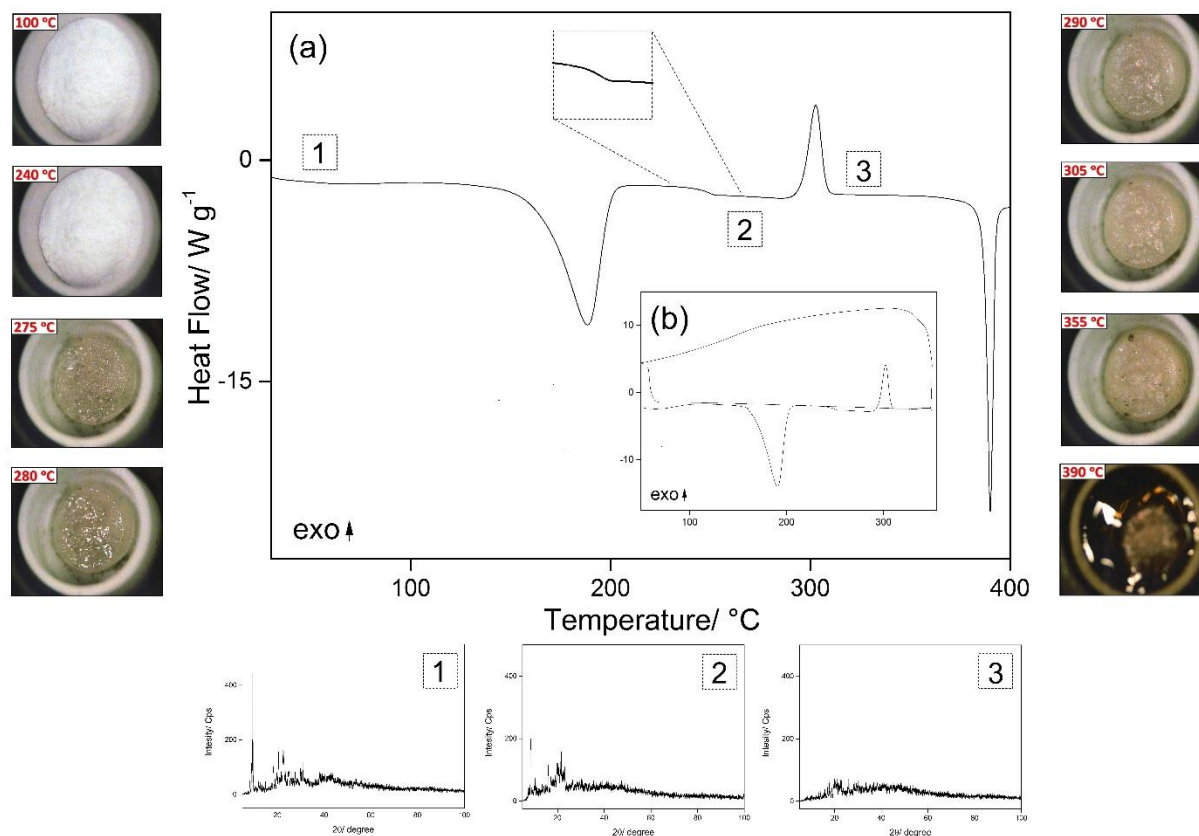
469

470 Figure 1: TG-DSC curves in air (a-d) and nitrogen (a*-d*) atmospheres of the compounds, where (a and
 471 a*) represents Mg; (b and b*) represents Ca; (c and c*) represents Sr and (d and d*) represents Ba.



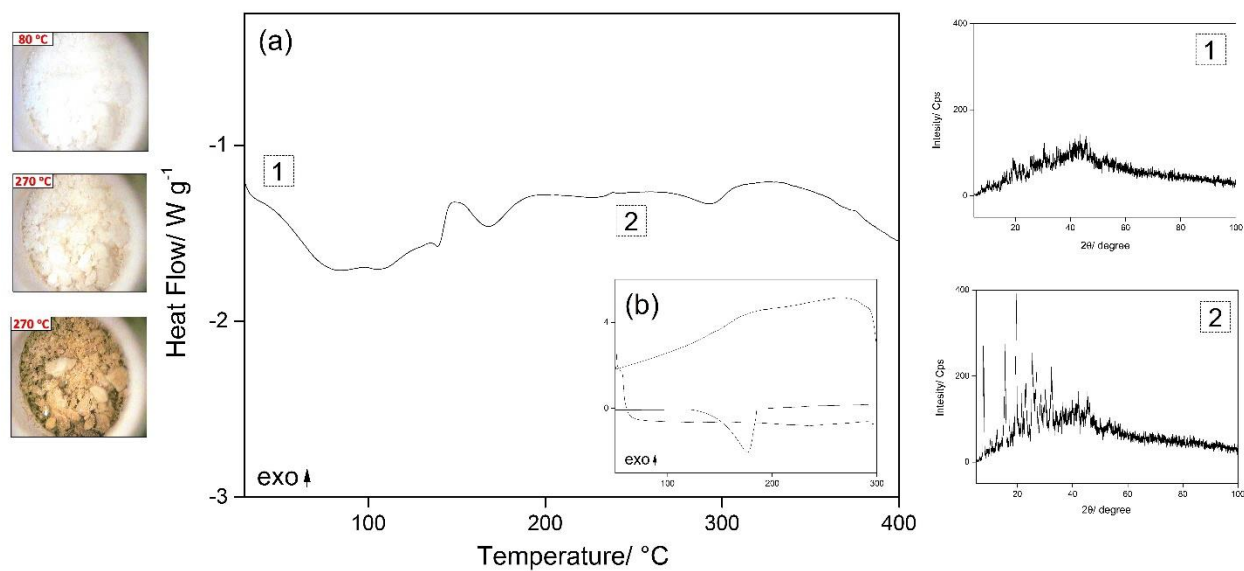
472

473 Figure 2: DSC curve, HSM micrographs and PXRD of magnesium picolinate.



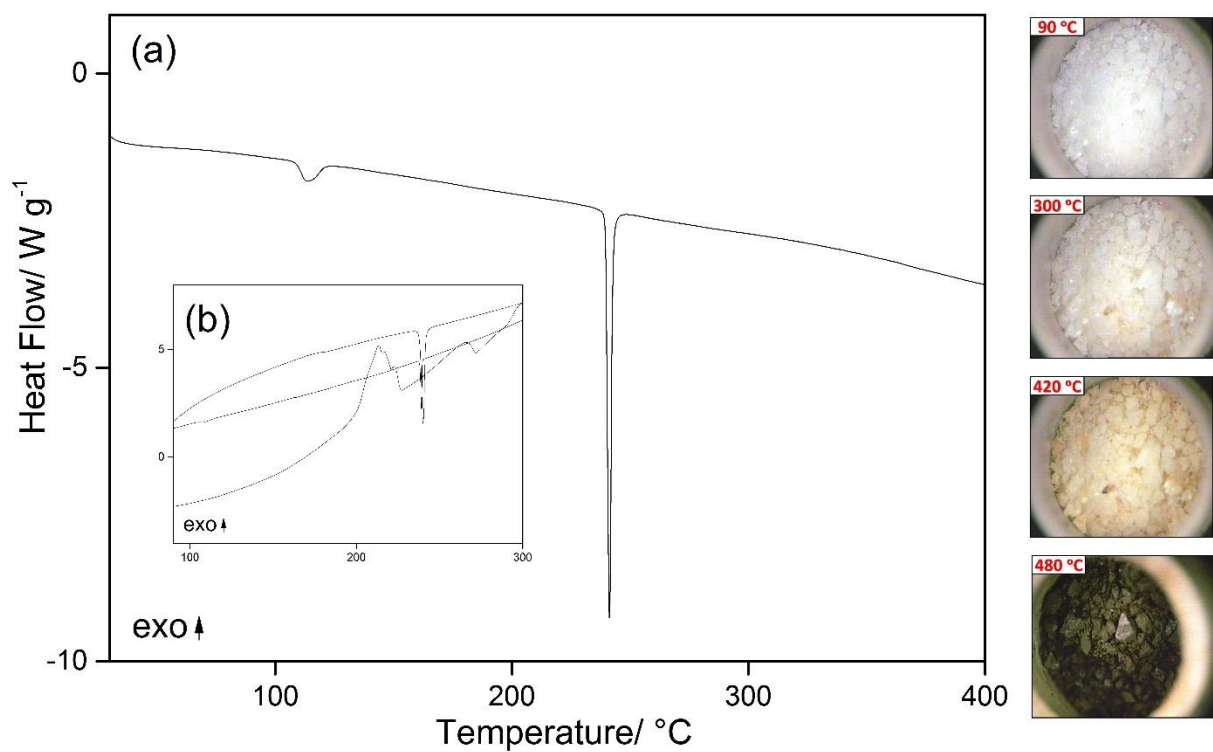
474

475 Figure 3: DSC curve (a), thermally cycled DSC experiment (b), HSM micrographs and PXRD of calcium
476 picolinate.

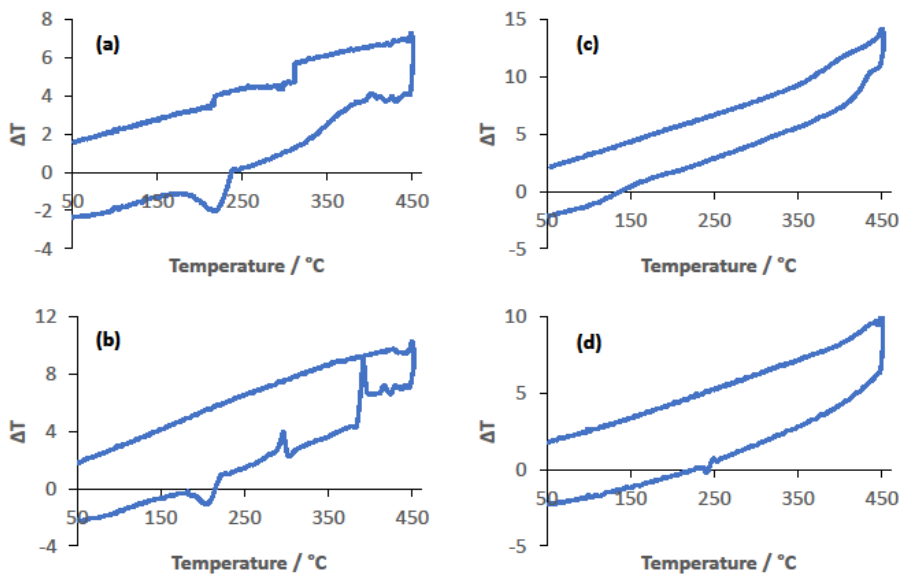


477

478 Figure 4: DSC curve (a), thermally cycled DSC experiment (b), HSM micrographs and PXRD of strontium
479 picolinate.

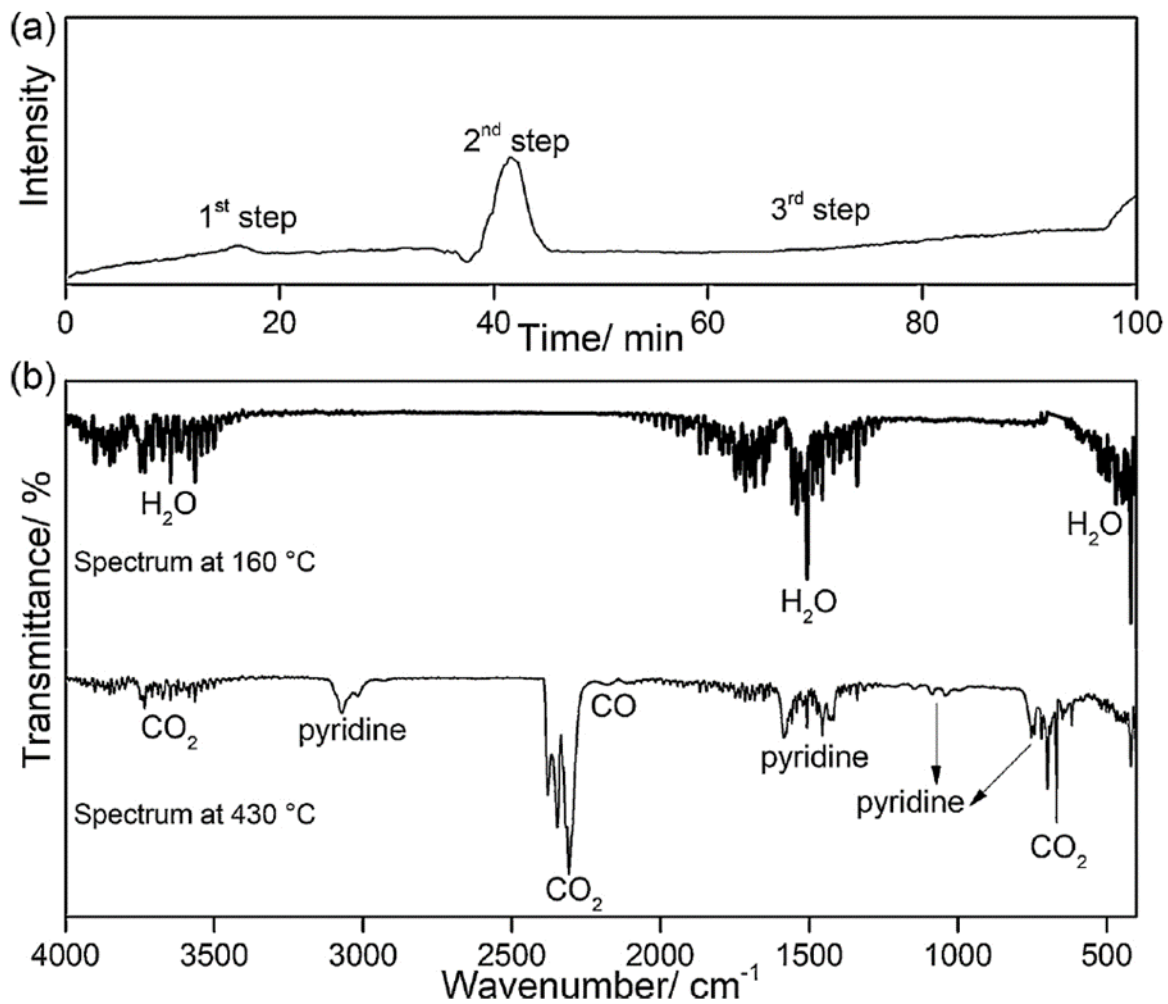


480
481 Figure 5: DSC curve (a), thermally cycled DSC experiment (b) and HSM micrographs of barium picolinate.



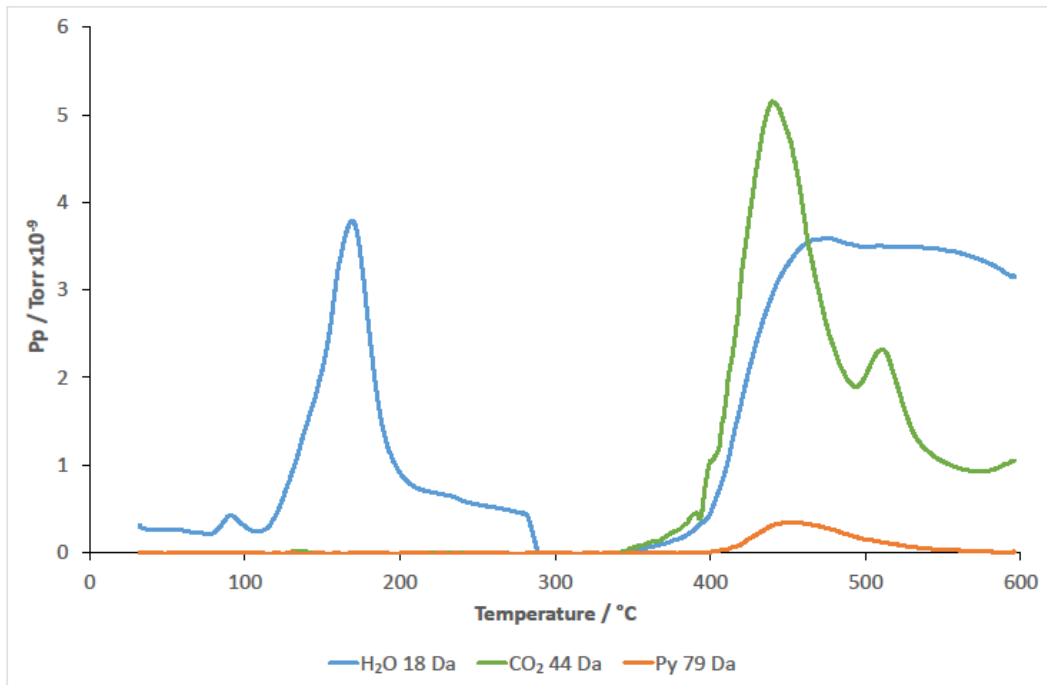
482

483 Figure 6: MWTA plots obtained for picolinate compounds. (a) magnesium picolinate, (b) calcium
484 picolinate, (c) strontium picolinate and (d) barium picolinate.



485

486 Figure 7: (a) Gram-Schmidt curve in nitrogen atmosphere; (b) IR spectra of gaseous products evolved
 487 during the decomposition of the magnesium picolinate.



488
 489 Figure 8: Mass spectra of the gaseous products evolved during the thermal decomposition of magnesium
 490 compound in helium atmosphere.

Table 1
 Analytical and thermoanalytical (TG^a) data for M(L)₂nH₂O compounds.

| Compounds | Metal oxide/ % | | | L (Lost)/ % | | Water/ % | | C/ % | | N/ % | | H/ % | | Final Residue |
|--|----------------|-------|-------|-------------|-------|----------|-------|-------|-------|-------|-------|-------|------|-------------------|
| | Calc. | TG | EDTA | Calc. | TG | Calc. | TG | Calc. | EA | Calc. | EA | Calc. | EA | |
| Mg(L) ₂ 2H ₂ O | 13.39 | 13.15 | 13.26 | 75.09 | 74.40 | 11.76 | 12.27 | 53.67 | 52.90 | 10.43 | 10.42 | 4.51 | 4.29 | MgO |
| Ca(L) ₂ 1H ₂ O | 18.41 | 18.45 | 18.48 | 75.67 | 75.32 | 5.92 | 6.23 | 47.67 | 48.02 | 9.27 | 9.38 | 3.34 | 3.11 | CaO |
| Sr(L) ₂ 1.5H ₂ O | 28.71 | 28.73 | 28.68 | 63.80 | 63.87 | 7.49 | 7.11 | 40.16 | 40.50 | 7.81 | 7.60 | 3.10 | 3.50 | SrO |
| Ba(L) ₂ | 50.27 | 50.66 | 50.60 | 48.55 | 48.12 | - | - | 36.90 | 37.15 | 7.17 | 7.31 | 1.96 | 2.11 | BaCO ₃ |

^a TG in air atmosphere, L = picolinate.