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STUDY OF THE ALKALINE EARTH METALS WITH 8-HYDROXYQUINOLINATE DERIVATIVES
Calcium complexes

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Abstract

Metal complexes of calcium with 5,7-dibromo, 7-iodo and 5-chloro-7-iodo-8-hydroxyquinolate were precipitated in aqueous ammonia and acetone medium, except for the solid state compound with 5,7-dichloro-8-hydroxyquinoline which hasn't been obtained under these conditions. The complexes obtained through the mentioned precipitation are $Ca[(C_9H_4ONBr_2)_2]_3 \cdot H_2O$, $Ca[(C_9H_5ONI)_2] \cdot 2H_2O$ and $Ca[(C_9H_4ONICl)_2] \cdot 2.5H_2O$. Their intermediate from the thermal decomposition found through TG/DTA curves in air indicated the presence of different kinds of calcium carbonates related to the reversibility and crystalline structure, depending on the original compounds. The initial compounds and the intermediate from the thermal decomposition were also characterized through IR spectra and X-ray diffraction.

Keywords: calcium, DTA, 8-hydroxyquinolinate derivatives, TG, thermal behavior

Introduction

The importance of metallic oxinates (8-hydroxyquinolinates) in analytical chemistry is well known [1–3]. The oxine and its derivatives have found extensive application as analytical reactant, that is, in absorption spectrophotometry, fluorimetry, extraction with solvent and chromatography of partition due its facility in form complexes with several metallic ions [4, 5].

Wendlandt and Horton studied the thermal behavior of 8-hydroxyquinoline, 5,7-dichloro, 2-methyl, 5-iodo, 5,7-dibromo and 5,7-diiodo-8-hydroxyquinoline and 8-hydroxyquinoline complexes with several metals as Cu, Zn, Cd and also of the 8-hydroxyquinoline derivative complexes with Th, Al and Cu. The peaks observed in DTA curves were attributed to dehydration, fusion and/or thermal decomposition of the chelate agents and to the thermal decomposition of the metallic complexes [6].

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Thermal behavior of metallic complexes of strontium [7], barium [8], and magnesium [9] with 5,7-dibromo, 5,7-dichloro, 7-iodo and 5-chloro-7-iodo-8-hydroxyquinoline were studied. It was proposed $SrBr_2$; mixture of $SrCl_2$, $SrCO_3$ and SrO; $SrCO_3$ and SrO as intermediates and residues from thermal decomposition of the compounds $Sr[(C_9H_4ONBr_2)_2]\cdot 2.5H_2O$; $Sr[(C_9H_4ONCl_2)(OH)]\cdot 1.5H_2O$; $Sr[(C_9H_5ONI)_2]\cdot 5H_2O$ and $Sr[(C_9H_4ONICl)(OH)]\cdot 1.25H_2O$, respectively. To the barium compounds, $Ba[(C_9H_4ONBr_2)_2]\cdot 1.5H_2O$; $Ba[(C_9H_4ONCl_2)(OH)]\cdot 1H_2O$; $Ba[(C_9H_5ONI)_2]\cdot 1H_2O$ and $Ba[(C_9H_4ONICl)_2]\cdot 5H_2O$, the intermediates and residues from thermal decomposition were, $BaBr_2$; mixture of $BaCO_3$, $BaCl_2$ and BaO; $BaCO_3$ and BaO; mixture of $BaCO_3$ and $BaCl_2$, respectively. The intermediates and residues from the thermal decomposition to the $Mg[(C_9H_4ONBr_2)_2]\cdot 2H_2O$ were a mixture of $MgBr_2$ and MgO; and to the $Mg[(C_9H_4ONCl_2)_2]\cdot 3H_2O$, $Mg[(C_9H_5ONI)_2]\cdot 2H_2O$ and $Ba[(C_9H_4ONICl)_2]\cdot 2.5H_2O$ the only residue obtained was the MgO.

In this work, the synthesis of the compounds of calcium with some 8-hydroxyquinoline derivatives are presented. The influence of halogen in the formation of the complexes and in the process of thermal decomposition were investigated.

Experimental

The reaction of the 8-hydroxyquinoline with the respective halogen in medium of acetic acid/water resulted in the ligands 5,7-dibromo, 5,7-dichloro and 7-iodo-8-hydroxyquinoline [10]; the reaction of 7-iodo-8-hydroxyquinoline with chlorine in aqueous medium resulted in 5-chloro-7-iodo-8-hydroxyquinoline. $C_9H_4ONBr_2$ (*m.p.*=199.1°C, N=4.56%; C=36.25%, H=1.41%); $C_9H_4ONCl_2$ (*m.p.*=182.1°C, N=6.51%; C=50.6%; H=2.37%) and C_9H_5ONI (*m.p.*=136.5°C, N=5.49%; C=33.3%; H=1.56%).

The solid state compounds of calcium with 8-hydroxyquinolinate derivatives were prepared by mixing, under constant stirring, the aqueous solution of the dehydrated calcium chloride with the acetone solution of the derivatives of 8-hydroxyquinoline. The pH was adjusted to 9 with concentrated aqueous ammonia solution under constant stirring and heating for one hour. After that solution was kept standby at room temperature until its complete sedimentation, then it was filtered and the precipitates washed with diluted aqueous ammonia solution several times in order to eliminate the excess of the ligands. Not only under these conditions described before but also under alcoholic medium, no kind of precipitate of calcium with $C_9H_4ONCl_2$ has been obtained. The obtained solid compounds were dried at 60°C and stored in a desiccator containing anhydrous $CaCl_2$.

The water molecule number was obtained from TG curves; 8-hydroxyquinoline derivative contents from both the TG curves and elemental analysis; and calcium from TG curves and ICP, Figs 1 and 2.

TG and DTA curves were obtained through TA Instruments, SDT 2960, on synthetic air atmosphere, and synthetic air/CO_2 mixture (70/30 and 50/50) with flux of 100 mL min^{-1}, heating rate of 20°C min^{-1}, samples mass around 8 mg and alumina crucible.

The calcium content present in the complexes was determined by using an inductively coupled plasma spectrometry (ICP), thermojarrel ash, model CID–DUO, line 189.989{136}.

Infrared absorption spectra were obtained in the region 4000–400 cm^{-1} by using a Nicolet Infrared Spectrophotometer model 400 with 4 cm^{-1} of resolution having the solid complexes been run as pressed pellets using KBr as diluent.

Elemental analysis data were obtained from CHNS-O, model Ea 1110 of the CE Instruments.

Results and discussion

TG-DTA curves

In the Figs 1 to 3 and Table 1 it is found TG-DTA curves and the data obtained from them for the compounds of calcium with 5,7-dibromo, 7-iodo, 5-chloro-7-iodo-8-hydroxyquinolinate in dynamic atmosphere of synthetic air and air/CO_2 mixture. Compounds in synthetic air atmosphere presented steps of dehydration followed by thermal decomposition/oxidation with formation of the $CaCO_3$ up approximately 660°C and then to CaO in temperature which were dependent on their initial compounds.

To the compound $Ca[(C_9H_4ONBr_2)_2]\cdot 3H_2O$, Fig. 1a, it was verified a first step of mass loss up to 206°C with loss of three molecules of water. Following, the thermal decomposition of anhydrous compound occur up to 660°C, with formation of $CaCO_3$,

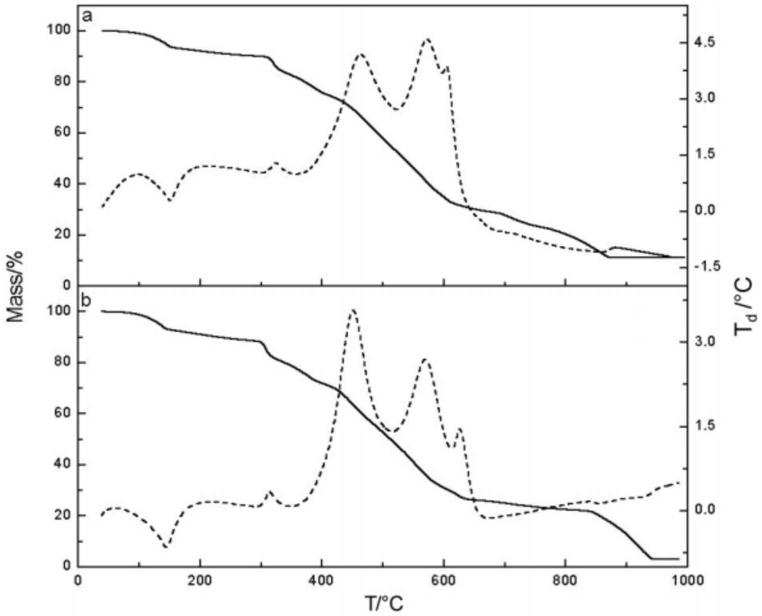

Fig. 1 TG and DTA curves of the compound: $Ca[(C_9H_4ONBr_2)_2]\cdot 3H_2O$: a – synthetic air and b – air/CO_2 mixture (70:30)

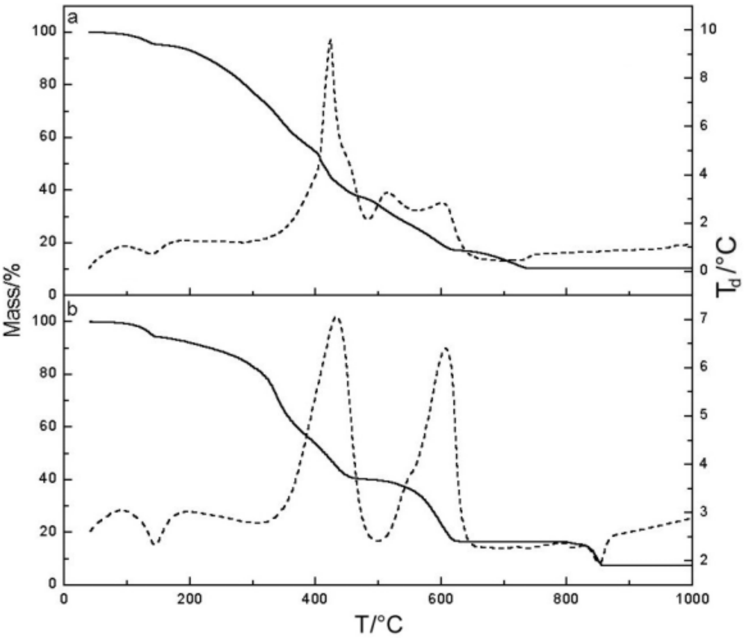

Fig. 2 TG and DTA curves of the compound: $Ca[(C_9H_5ONI)_2]·2H_2O$: a – synthetic air and b – air/CO_2 mixture (70:30)

which decomposes in two steps; the first step occurs up to 780°C and the second up to 880°C, probably due to two kinds of carbonates. However, X-ray of residues indicated no crystalline structures.

TG curve in air/CO_2 atmosphere (70/30), Fig. 1b, shows similar behavior up to 650°C when is obtained mixture of approximately 14.6% of $CaCO_3$ and 5.4% of $CaBr_2$. The $CaCO_3$ is decomposed to CaO in two steps between 650 and 950°C, in which the last step present the total vaporization of $CaBr_2$ [11]. DTA curves shows an endothermic peak around 140°C related to the dehydration observed in the first step from TG curve. It has been verified an exothermic peak between 300 and 640°C related to the thermal decomposition/oxidation of the ligand with formation of $CaCO_3$ and $CaBr_2$. The thermal decomposition of $CaCO_3$ to CaO and vaporization of $CaBr_2$ can be observed through two endothermic broad peaks between 800 and 1000°C to air/CO_2 atmosphere. To the synthetic air atmosphere a broad peak between 700 and 900°C, due to thermal decomposition of $CaCO_3$ to CaO, is observed.

To the $Ca[(C_9H_5ONI)_2]·2H_2O$, five steps of mass losses were verified, Fig. 2, to synthetic air and air/CO_2 atmospheres. The first one can be observed up to 150°C, being referent to the dehydration of the compound which can be confirmed through the endothermic peak around 140°C in DTA curves. Following, steps of thermal decomposition of anhydrous compound with formation of reversible $CaCO_3$ (calcite from rhombohedral system [14], X-ray Fig. 4a) were verified as observed by the displacement of temperature

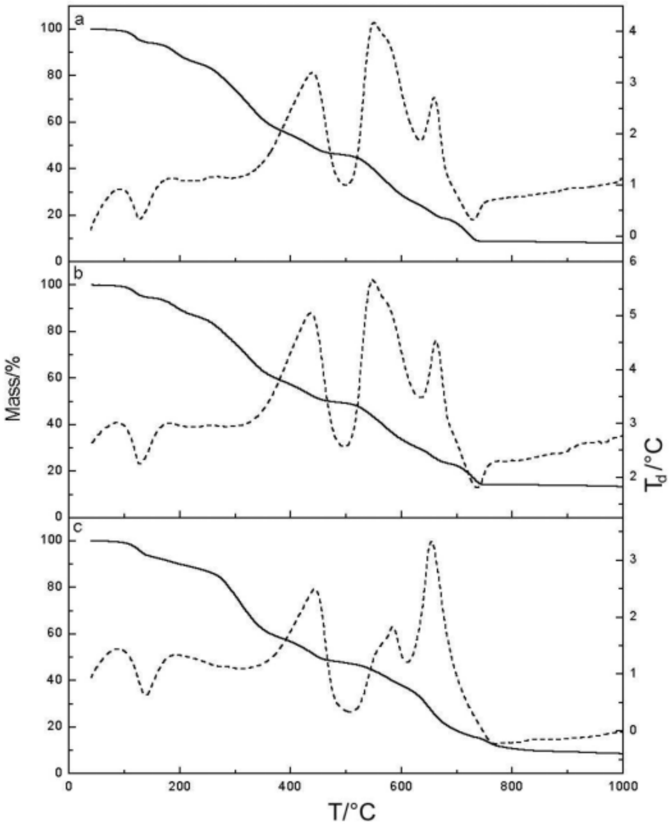

Fig. 3 TG and DTA curves of the compound: Ca[$(C_9H_4ONICl)_2$]·$2.5H_2O$: a – synthetic air, b – air/CO_2 mixture (70:30) and c – air/CO_2 mixture (50:50)

higher than 100°C in air/CO_2 atmosphere. Under these conditions some alteration in thermal behavior can be observed in intermediate steps of thermal decomposition/oxidation. In DTA curves it can be verified the displacement of the endothermic peak due to $CaCO_3$ decomposition from 720 (air) to 850°C (air/CO_2).

Table 1 Metal, ligand and water contents from analytical and thermal analytical (TG) data

Compound	Calcium/%			Water/%		Ligand/%	
	theor.	TG	ICP	theor.	TG	theor.	TG
Ca[$(C_9H_4ONBr_2)_2$]·$3H_2O$	5.74	6.43	5.67	7.74	7.49	84.22	83.40
Ca[$(C_9H_5ONI)_2$]·$2H_2O$	6.50	7.14	6.75	5.85	6.00	85.05	86.73
Ca[$(C_9H_4ONICl)_2$]·$2.5H_2O$	5.77	5.86	5.39	6.49	6.50	85.43	85.35

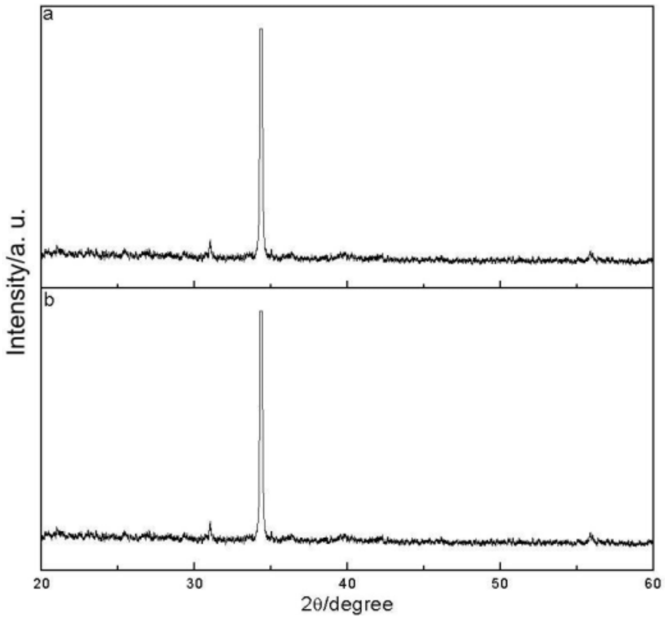

Fig. 4 XRD patterns of the complexes residue: a – Ca[(C_9H_5ONI)$_2$]·2H_2O at 700°C and b – Ca[(C_9H_4ONICl)$_2$]·2.5H_2O at 700°C

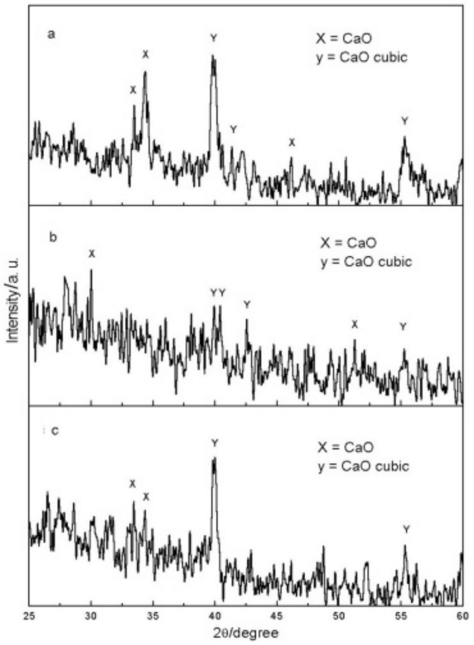

Fig. 5 XRD patterns of the complexes residue: a – Ca[($C_9H_4ONBr_2$)$_2$]·3H_2O at 1050°C; b – Ca[(C_9H_5ONI)$_2$]·2H_2O at 900°C and c – Ca[(C_9H_4ONICl)$_2$]·2.5H_2O at 1200°C

Table 2 Results from elemental analysis

Compound	C/%		H/%		N/%	
	theor.	exp.	theor.	exp.	theor.	exp.
$Ca[(C_9H_4ONBr_2)_2]·3H_2O$	31.0	31.2	2.02	2.47	4.01	4.49
$Ca[(C_9H_5ONI)_2]·2H_2O$	35.1	35.4	2.29	2.47	4.55	4.05
$Ca[C_9H_4ONICl)_2]·2.5H_2O$	31.2	31.1	1.89	2.56	4.04	3.93

TG curves of $Ca[(C_9H_4ONICl)_2]·2.5H_2O$ presented the first step of mass loss up to 145°C due to the dehydration of the compound with loss of two and half molecules of water. After this, the loss of ligand molecule occurs, once the remaining ligand decomposes in two steps with formation of $CaCO_3$ at 692°C in both air and air/CO_2 atmospheres.

Table 3 Thermal analytical parameters observed through TG-DTA curves obtained at 20°C min^{-1} up to 1000°C, under dynamic synthetic air atmosphere (100 mL min^{-1}) and using alumina crucible, for calcium compounds

Compound	TG curve		DTA curve	
	mass loss/%	ΔT/°C	endothermic/°C	exothermic/°C
$Ca(C_9H_4ONBr_2)_2·3H_2O$	7.50	40–198	140	–
	67.5	198–656	–	300 442 520–550
	21.3	660–959	650	–
$Ca(C_9H_5ONI_2)_2·2H_2O$	6.00	40–153	140	–
	77.63	153–640	–	429 513–605
	9.10	640–938	720	–
$Ca(C_9H_4OICl)_2·2.5H_2O$	6.50	40–144	130	–
	45.16	144–475	–	438
	31.62	475–693	–	550–663
	9.77	693–800	730	–

Despite the fact the $CaCO_3$ shows the same rhombohedral structure, X-ray Fig. 4b, it is irreversible as we can see through the small displacement in the temperature of the thermal decomposition to CaO even when the air/CO_2 relationship passed from 70/30 to 50/50.

DTA curves presented an endothermic peak at 130°C, attributed to the dehydration of the compound. Up to 250°C it was verified the existence of exothermic peaks up to 550°C, which were ascribed to the thermal decomposition/oxidation of the anhydrous compound with formation of $CaCO_3$ which decomposes to CaO as verified though an endothermic peak around 730°C in both air and air/CO_2 atmospheres.

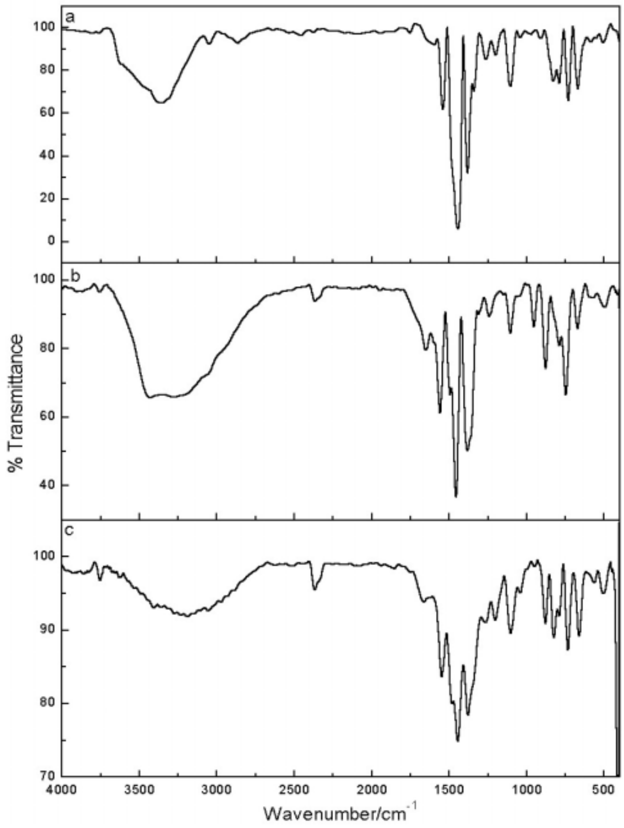

Fig. 6 IR Spectra of the complexes: a – $Ca[(C_9H_4ONBr_2)_2]\cdot 3H_2O$; b – $Ca[(C_9H_5ONI)_2]\cdot 2H_2O$ and c – $Ca[(C_9H_4ONICl)_2]\cdot 2.5H_2O$

The final residues, CaO, which came from the thermal decomposition of these compounds, presented themselves as a mixture of cubic and other undefined system [14], Fig. 5.

The absence of iodo and chloro in the residues formed at 680°C and 1050°C was confirmed through specific qualitative tests [12].

IR spectra

The IR absorption spectra, Fig. 6, show characteristic bands [13] to each complex obtained, Fig. 5. The compound $Ca[(C_9H_4ONBr_2)_2]\cdot 3H_2O$ presents medium IR bands at 730 and 669 cm^{-1} corresponding to the stretching mode of the equatorial and axial C–Br bond, respectively. To the $Ca[(C_9H_5ONI)_2]\cdot 2H_2O$ the bands at 730–600 cm^{-1} region are related to the stretching mode of the C–I bond. When the calcium is presented as 5-chloro-7-iodo-8-hydroxyquinoline, the same behavior is verified, but with medium IR bands at 650–500 cm^{-1}, attributed to the stretching mode as well as axial C–Cl and equatorial C–I bonds.

The strong intensity band in 1500–1350 cm^{-1} region appears in all spectra and they are attributed to the stretching of the C–O and C–N bonds, indicating that the calcium is coordinated through the oxygen and nitrogen atoms from the 5,7-dibromo, 7-iodo and 5-chloro-7-iodo-8-hydroxyquinoline.

Conclusions

The presence of halogen in the ligand causes changes in the thermal decomposition of the complexes, depending on the atmosphere. The structure and thermal decomposition of $CaCO_3$ obtained in intermediate residues range significantly depending on the compounds from which they were origin. However, the final residue formed through these techniques are similar with small alteration in their crystalline structures.

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References

1 V. Alexeév, Análise Quantitativa, Livraria Lopes da Silva, 3ª Edição, Porto 1983.
2 F. J. Welcher, Organic Analytical Reagents, Van Nostrand, New York 1947.
3 S. Chaberek and A. E. Martell, Organic Sequestering Agents, Wiley, New York 1959.
4 H. Irving and A. R. Pinnington, J. Chem. Soc., Part I (1957) 285.
5 M. P. Bratzel, J. J. Aron and J. D. Winefordner, Anal. Chem., 44 (1972) 1240.
6 W. W. Wendlandt and G. R. Horton, Anal. Chem., 34 (1962) 1098.
7 C. T. R. Guerreiro, C. A. Ribeiro, M. S. Crespi and C. Torres, J. Therm. Anal. Cal., 56 (1999) 519.
8 C. A. Ribeiro, M. S. Crespi, C. T. R. Guerreiro and L. S. Guinesi, J. Therm. Anal. Cal., 64 (2001) 637.
9 C. T. R. Guerreiro, C. A. Ribeiro, M. S. Crespi and C. Torres, J. Therm. Anal. Cal., 67 (2002) 419.
10 C. T. Ramelo, R. Faez, C. A. Ribeiro and M. Spirandeli Crespi, Eclética Química, 20 (1995) 49.
11 P. Pascal, Nouveau Traité de Chimie Minérale, Tome IV; Masson et Cie; Paris 1958.
12 A. I. Vogel, Textbook of Macro And Semimicro Qualitative Inorganic Analysis, 5th Edition, Longman, London and New York 1979.
13 A. D. Cross and R. A. Jones, An Introduction to Practical Infra-Red Spectroscopy, 3rd Edition, Butterworths, London 1969.
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