

# Determination of the optimum parameters in the high resolution thermogravimetric analysis (HRTG) for cementitious materials

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**Abstract** In this article, the methodology to implementation of high resolution thermogravimetric analysis (HRTG) for construction materials like Portland cement pastes is presented. The aim of this technique is to make easier the identification of the decomposition reactions that frequently are overlapping on conventional thermogravimetric analysis (TG) like is the case of some mineral phases in the cement pastes. The optimum parameters related to sample mass and purge flow gas were established. It is necessary carried out the analysis with high quantity of sample (60 mg in this case) and without purge gas in order to get better results and excellent reproducibility. The tests have average heating rate higher than  $3\text{ °C min}^{-1}$  in the temperature range studied ( $35\text{--}300\text{ °C}$ ), showing that the HRTG is not time-expensive technique.

**Keywords** High resolution thermogravimetry · Portland cement · Decomposition · Variable heating rate

## Introduction

Thermogravimetric analysis (TG) and its first derivative (DTG) and differential thermal analysis (DTA) are technical very employed in the identification of the mineral phases or compositional analysis in materials such as clay, plaster, limes, gypsum and cements, among others [1–5]. In

addition, this technique enables the quantification of the minerals present determining the mass loss by the different decomposition reactions that may occur, such as dehydration, combustion, dehydroxilation, etc. [6].

The great disadvantage of this technique is that is very common to find that different minerals have very close change phases or decomposition temperature, with overlapping peaks in the DTG curves.

To resolve this phenomenon, usually the heating rate is diminished ( $0.5\text{ °C min}^{-1}$  for example), looking for quasi-isothermal conditions during the reactions of interest. Of this way it can get a better resolution in the thermogram. This improvement in resolution occurs if the rate of reaction and the respective activation energies are sufficiently different [7, 8]. The problem is that since the heating rate is constant the analysis costs rise significantly, by hours of use of the equipment, making the technique economically unfeasible.

These thermal analysis techniques (DTA, TG, and DTG) have been also used to analyze hydrated cement pastes [9, 10]. In these materials, one of the most important analytical parameters is the water released from calcium hydroxide dehydroxilation. In this case, these analyses are used to evaluate cement-based materials containing pozzolanic additions. The pozzolanic activity is measured from the calcium hydroxide consumption that these materials present forming similar hydrated products to those produced from the hydration of cement component substances [11–13].

When a sample of hydrated Portland cement paste is analyzed, “minerals” as the tobermorite, ettringite and gypsum often are in overlapping peaks in the temperature interval  $100\text{--}180\text{ °C}$ , because their reactions occur practically consecutive and the constant heating rate of the conventional TGA impedes their differentiation. In these cases, in DTG curve is common to find peaks widened or

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shoulders because signal (mass loss rate) between two processes fails to return to the base line (null transformation rate), which prevents accurate recognition of phases and quantification of these.

To resolve these difficulties have been found very few references. Dweck et al. [14] present a method to study cement hydration at ambient temperatures by using a micro processes non-conventional DTA system.

Criado et al. [15] develop an alternative method applied to inorganic products, called “constant rate thermal analysis” (CRTA) that implies achieving a temperature profile at which the reaction rate remains constant all over the process at a value previously selected by the user.

The overlapping peaks could be resolved using the maximum resolution (MaxRes<sup>TM</sup>) or High Resolution (Hi-Res<sup>TM</sup>) modules available in machines of some brands thermal analysis software. This specific software enables the compositional analysis faster without losing resolution [7, 16]. These techniques have been used successfully to characterization of different materials such as hydrotalcites, polyimides, and diesel fuel additives [17–20].

Construction materials, like the Portland cement pastes, are particularly complex to perform their TG because the reaction products are not stoichiometric compounds. This fact, coupled with the overlapping in some of the decomposition processes, makes to these materials perfect candidates to be scanned using high resolution thermogravimetric analysis (HRTG) technique, but little has been written about them in this theme.

## Basic concepts

High resolution thermogravimetric analysis technique enables the TG analysis in a dynamic manner because the heating rate of the sample, depending on its weight loss, can be scheduled regardless of the processes involved and of its kinetics [1]. In this way, it is possible to achieve shorter testing time with improved resolution in comparison to the conventional TG. Software parameters are defined as:

- Minimum and maximum rates of heating (in  $^{\circ}\text{C min}^{-1}$ ,  $V_{\min}$  and  $V_{\max}$ )
- Highest and lowest mass loss threshold (in  $\mu\text{g s}^{-1}$ ,  $W_{\max}$ ,  $W_{\min}$ ) to modify the heating rate
- Value factor ( $f$ ) and timeout ( $t$ )
- Temperature range.

Essentially software enables begin with maximum heating rate ( $V_{\max}$ ) and when the lowest mass loss threshold ( $W_{\min}$ ) is exceeded then the heating rate decreases in a given factor ( $f$ ), meets timeout ( $t$ ) and again evaluates the progress of mass loss. If the condition is preserved, the heating rate is again dropped in the same factor. This

continues until the minimum established heating rate ( $V_{\min}$ ) is reached or when maximum speed mass loss ( $W_{\max}$ ) threshold value is exceeded. The resulting temperature program is a set of dynamic segments [7]. Thus, decomposition steps observed in the thermogram are more vertical and the overlapping decreases among consecutive and close process, since the decomposition occurs almost in quasi-isothermal conditions, facilitating significantly its evaluation [1].

High resolution thermogravimetric analysis technique and all modifications developed to improve resolution, based on the heating rate decreasing presented as main constraint that events cannot be separated if the second overlapped reaction activation energy is much larger than the first one. In these cases, methods, or conditions must be modified, such as to change gas or pressure [7].

## Methods and materials

Spanish Portland cement (CEM I 52.5R) paste samples blended with 10% of a high reactivity siliceous pozzolan (Nyasil) to 28 days of normal curing were analyzed for this study. Addition of this pozzolan lets to generate a large amount and diversity of hydrated products. The pastes were prepared with a relationship water/binder 0.4 and pozzolan/cement ratio was 1/9. At 28 days of curing at  $20 \pm 2^{\circ}\text{C}$ , the samples were ground in the presence of acetone, filtered and the resulting solid dried in oven at  $60^{\circ}\text{C}$  for 30 min.

In a TGA 850 Mettler-Toledo the samples were analyzed, 100  $\mu\text{L}$  with perforated sellable lid aluminum crucibles (allowing that into the crucible a self-generated atmosphere to be produced from water vapor released by the sample) and dry  $\text{N}_2$  as purge gas were used.

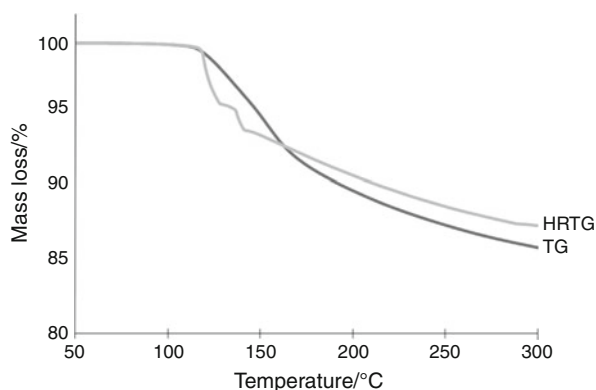
Followings parameters to perform tests on the thermogravimetry machine were chosen:

- Minimal heating rate,  $V_{\min}$ :  $0.5^{\circ}\text{C min}^{-1}$
- Maximum heating rate,  $V_{\max}$ :  $10^{\circ}\text{C min}^{-1}$
- Maximum mass loss threshold,  $W_{\max}$ :  $3 \mu\text{g s}^{-1}$
- Minimum mass loss threshold,  $W_{\min}$ :  $1 \mu\text{g s}^{-1}$
- Factor,  $f$ : 2
- Timeout,  $t$ : 6 s
- Temperature range,  $35\text{--}300^{\circ}\text{C}$ .

## Results and discussion

### Comparison between HRTG and conventional TG

Figure 1 presents the curves to a same sample analyzed by conventionally TG ( $10^{\circ}\text{C min}^{-1}$ ) and by HRTG, with the



**Fig. 1** Thermogravimetric analysis curves; conventional (TG) versus high resolution (HRTG)

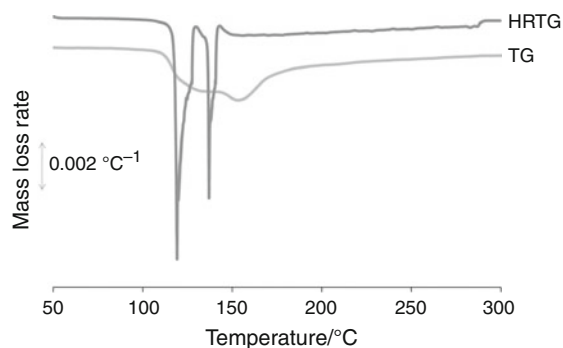
same conditions: 60 mg sample weight, sealed aluminum crucible of 100  $\mu\text{L}$  with pinholed cover lid and 75  $\text{mL N}_2 \text{ min}^{-1}$  purge gas.

There is a clear difference between the resolutions of both curves. In TG curve, the mass loss is practically constant shown only a slope change meanwhile that in the HRTG curve there are two slope changes, it shows different decomposition reactions in the temperature range evaluated, that is, this method detects up to two processes in the 100–200  $^\circ\text{C}$  range. The HRTG allows higher resolution of the events that occur during the heating of the sample.

The differences between two methods are clearer in the corresponding derivative DTG curves (Fig. 2).

In HRTG curves (Figs. 1, 2) the decompositions (dehydration and dehydroxylation) that occur in the sample are better resolved, for the range of studied temperature two clearly distinguishable peaks are obtained (Fig. 2). The conventional TG displays only one peak ( $T \approx 150^\circ\text{C}$ ) with a shoulder to the left ( $T \approx 130^\circ\text{C}$ ).

This behavior is because in high-resolution technique the temperature remains almost constant during decomposition, for this reason, decomposition events have more possibilities to be detected and differentiated.



**Fig. 2** Comparison between a conventional TG test and HRTG: derivative curves

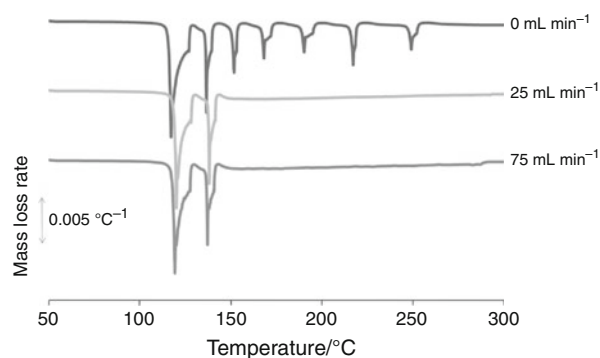
### Influence of the purge gas flow in HRTG

Figure 3 shows changes in the DTG curves obtained with high resolution varying purge gas flow. The gas changes were from 0  $\text{mL min}^{-1}$  as many as 75  $\text{mL min}^{-1}$  of  $\text{N}_2$ . All the others test condition were equals.

In the TG derivate curve (Fig. 2) and when purge gas was used (Fig. 3), after 200  $^\circ\text{C}$  there are not any peaks.

When the gas flow is null (Fig. 3), the resolution increases and events of decomposition at temperatures higher than 150  $^\circ\text{C}$  may be detected. This fact is related to the formation of a self-generated atmosphere of water steam in the crucible. When there is gas flow, the gas running directly over the pinhole sealed lid of the crucible, and drag the steam generated in the decompositions. Thereby the pressure of water vapor in the interior of the crucible is reduced and not allow stabilize the different hydrates still existing in the sample. However, when no purge gases, the pressure of water vapor in the interior of the crucible is higher. This fact allows stabilize more hydrates remnants, to the point that it can see up to 5 peaks more than in the previous cases.

Table 1 shows the temperatures of the first two peaks in the curves. Elimination of the gas flow makes decomposition reaction is detected at temperatures slightly lower. Signals integration allows quantifying the amount of evaporated material. Mass loss in the first two reactions in the trial without purge gas is slightly greater.



**Fig. 3** Variation of the DTG-HRTG curves with the purge gas flow

**Table 1** Variation of the DTG-HRTG curves with the purge gas flow

Purge gas flow/ $\text{mL min}^{-1}$ of $\text{N}_2$	Position peak 1/ $^\circ\text{C}$	Position peak 2/ $^\circ\text{C}$	Mass loss/%
0	117.2	136.7	6.27
25	120.2	138.2	5.83
75	119.3	137.2	6.10

In accordance with the preceding remarks, we recommend to make the tests without purge gas

Influence of the sample mass on the thermograms resolution

Figures 4 and 5 are, respectively, TG and DTG curves obtained applying the HRTG technique based on the variation mass of the hydrated cement. The same sample, under the same conditions (no purge gas), varying the mass of sample was analyzed. The mass increased from  $10 \pm 1$  (sample c10) up to  $60 \pm 1$  mg (sample c60).

An increase in the resolution of the thermograms insofar increasing the mass of the sample was evidenced. Samples with 40, 50, and 60 mg have great similarity especially in the first two peaks (Fig. 5) which are the mainly for these samples. To corroborate this total mass loss due to the decomposition of the sample until a temperature evaluated was calculated (Fig. 6).

Mass loss shows an important error in the sample 10 mg (4.7%), which indicates that this amount is not appropriate for these analyses. Thereafter, the difference in weight is minimal (0.84%), being essentially equal the percentage in the mass loss to the samples 50 mg and 60 mg with a difference of 0.2%.

From the curve for the sample c60, can be calculated (Table 2) Mass losses associated (in percentage,  $X_i$ ) to each peak as well as temperatures of maximum mass loss rate

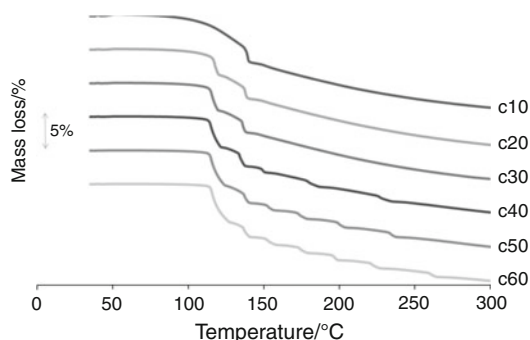


Fig. 4 Changes in the thermogravitic curves HRTG with the variation of the sample mass

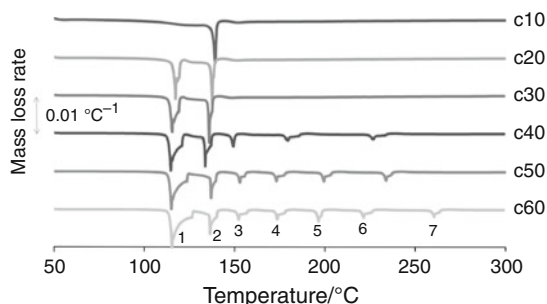


Fig. 5 Changes in the DTG-HRTG curves with the variation of the samples mass

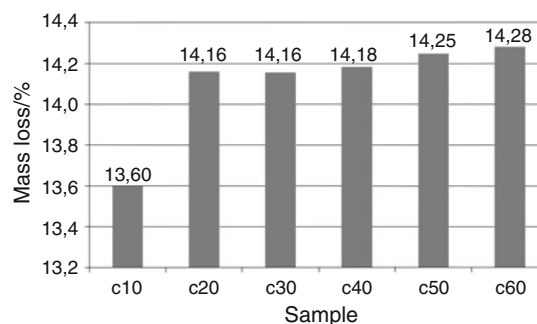


Fig. 6 Total mass loss by varying the mass of the sample

Table 2 Parameters of the peaks of the DTG curves

Sample	Peaks	$T_i^{max}/^{\circ}C$	$T_a/^{\circ}C$	$T_b/^{\circ}C$	$X_i/^{\circ}C$	
C <sub>10</sub>	1					
	2	139.45	130	142	3.34	
	C <sub>20</sub>	1	117.24	100	120	3.43
		2	137.66	120	140	3.58
	C <sub>30</sub>	1	115.43	100	120	3.85
2		135.88	120	140	3.31	
C <sub>40</sub>	1	114.75	100	120	3.97	
	2	133.76	120	138	3.23	
	3	149.23	138	151	0.93	
	4	178.98	151	187	2.17	
	5					
C <sub>50</sub>	6	226.25	187	235	2.15	
	1	114.95	100	125	5.1	
	2	136.89	125	140	2.51	
	3	152.83	140	158	1.18	
	4	172.97	158	180	1.27	
	5	199.28	180	205	1.27	
C <sub>60</sub>	6	233.74	205	240	1.42	
	1	115.34	100	127	5.55	
	2	136.38	127	142	2.22	
	3	152.06	142	158	1.13	
	4	173.61	158	180	1.23	
	5	196.32	180	200	1.05	
	6	221.35	200	227	1.19	
7	260.28	227	265	1.27		

(in  $^{\circ}C$ ,  $T_i^{max}$ ). Mass losses  $X_i$  are calculated for each peak since the end of the previous event ( $T_a$ ) until the completion of the event considered ( $T_b$ ).

Table 2 shows that except for C10, in all other cases integration intervals remain very similar, i.e. that each process begins and ends for similar temperature. Beside, the position of the peaks ( $T_i^{max}$ ) just varies and mass loss values change with the mass because the resolution is greater. Loss to peak 1 is increasing at the expense of the 2

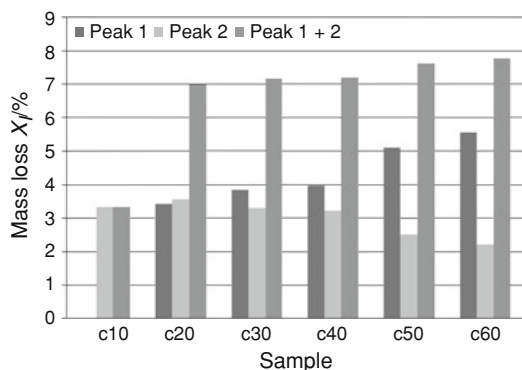


Fig. 7 Mass loss of the samples in the two first peaks (HRTG)

peak, but the sum of two mass loss remain constant (Fig. 7).

Figure 8 shows the variation in temperature with the time, for this same set of samples. In these curves the different changes in speed of warming can be viewed. Maximum gradient levels correspond to the maximum speed  $V_{max}$  and sloping minimum to  $V_{min}$ .

The software changes the rate of increase in temperature on the loss of the sample mass. Thus, reactions involving little variation in the mass are almost imperceptible to the computer, so the heating rate tends to be constant and maximum (high slope in the graph) and when has been an increase in the mass loss, product of the breakdown of any constituent phases of the sample, the heating rate decreases until the minimum. In the sample c60, equipment can detect a high number of decomposition reactions and even evaluates them to a rate less heating because in each weight loss is more noticeable.

The average rate of warming for each test can be calculated from the curves shown in Fig. 8. Thus, for trials showing higher resolution (c40, c50 and c60) test times are between 3550 s (something less than 1 h) and the 5080 s (less than hour and a half). Those times, taking into account the range of the test temperature is 35–300 °C, give rise to

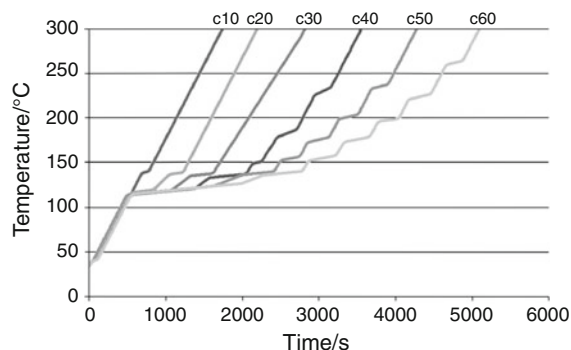


Fig. 8 Variation in the temperature samples with the time

very high heating speeds: c40, speed is 4.5 °C min<sup>-1</sup> for c50 is 3.7 °C min<sup>-1</sup> for c60 is 3.1 °C min<sup>-1</sup>.

From these results to work with the maximum possible mass is recommended. In the studied case for hydrated cement samples working with 60 mg is suggested.

Reproducibility of results

Figure 9 shows the comparison between two curves obtained with the same sample and the same parameters of TG (60 ± 1 mg, without purge gas).

The same number of events is detected, encountered with slight differences in the temperature corresponding to the maximum mass loss rates ( $T_i^{max}$ ). Table 3 shows the values of  $T_i^{max}$  as well as mass loss rates ( $P_i^{max}$ ) associated with each peak and the percentages of mass loss  $X_i$  attributed to each peak.

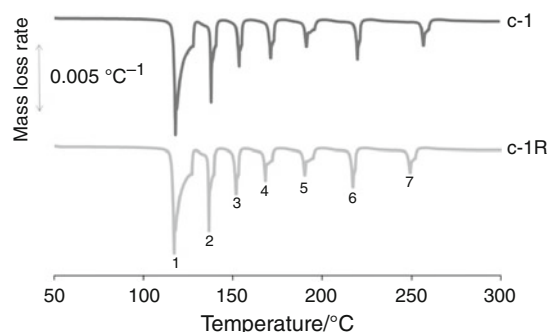


Fig. 9 Test reproducibility (HRTG) in samples of hydrated cement

Table 3 Parameters of the decompositions in HRTG curves

Peaks	C-1			C-1R		
	$T_i^{max}$	$P_i^{max}$	$X_i$	$T_i^{max}$	$P_i^{max}$	$X_i$
1	117.9	54.3	4.8	117.1	39.4	4.5
2	137.8	45.5	1.4	136.6	35.3	1.5
3	153.3	15.8	1.2	151.6	22.2	1.1
4	170.9	16.6	1.1	167.9	20.0	1.1
5	191.0	16.1	1.1	190.0	13.6	1.2
6	219.6	15.8	1.1	217.0	23.1	1.0
7	256.2	11.5	0.9	248.8	15.0	0.8
Total			12.8			12.5

$T_i^{max}$  and  $X_i$  have practically equal values for the two curves (C-1 and C-1R). However,  $P_i^{max}$  has slight differences. For these reasons, it is possible assert that for studied material, the reproducibility is very high in size and position of the peaks for proposed parameters

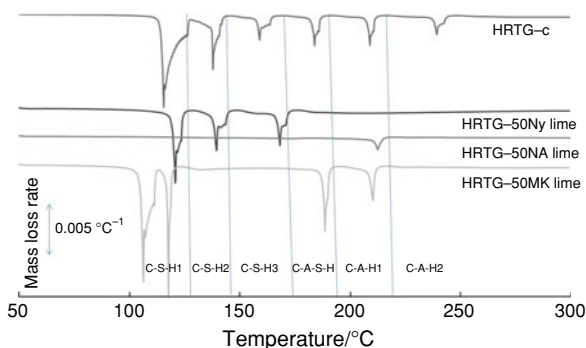
## Identification of the peaks

To identify the peaks present in the DTG curves of HRTG obtained of samples of cement with 10% of Ny, reagent-grade lime with 50% of substitutions by Nyasil (Ny), metakaolin (MK), and nanoalumina (NA) were run, with the optimal parameters found, in order to locate the decomposition temperatures of calcium silicate hydrate (C-S-H: tobermorite), calcium aluminosilicate hydrate (C-A-S-H: hydrated gehlenite), calcium aluminate hydrate (C-A-H). The comparisons are presented at Fig. 10.

DTG curve at the top of Fig. 10 corresponds to the sample of cement with Ny and 14 days of curing, while the three curves at the bottom are the samples of lime with different replacement materials and the same curing time.

Based on these results, we can say that the first three peaks at HRTG-c curve, low to high temperature, correspond to decomposition of calcium silicates hydrate (C-S-H), the fourth peak corresponds to calcium aluminosilicates hydrate (C-A-S-H) and the last two to calcium aluminates hydrate (C-A-H). These statements is based on that the three first peaks of the cement sample coincide in position with the peaks present in the sample of lime with Ny where can just be calcium silicates hydrate, in the temperature range evaluated. The fifth peak, is on the same position that the unique peak at DTG curve of the sample of lime with nanoalumina where can just to form calcium aluminate hydrate. In the case of a sample of lime with metakaolin is expected to form calcium silicates hydrate, calcium aluminosilicates hydrated and calcium aluminates hydrate, there are two peaks in this sample that have a great overlap with the proposed peaks to the other samples as C-S-H and C-A-H, so the additional peak would be for the C-A-S-H. The final decomposition process can be associated to C-A-H by the temperature of dehydration suggested to him by various authors [2].

C-S-H<sub>2</sub> peak coincides with the peak identified by several authors [1, 2] for the dehydration of ettringite, so it is possible to have an overlap of these two phases.



**Fig. 10** Identification of peaks obtained with the HRTG

## Conclusions

The technique of HRTG is a highly efficient method to separate reactions of decomposition that overlap in thermal analysis of materials as hydrated Portland cement. This technique allows identifying different mineral phases present in the samples (C-S-H, C-A-S-H, C-A-H).

The resolution obtained is heavily dependent of the sample mass. We recommend working with 60 mg for Portland cement pastes for the used equipment. The resolution is significantly better when purge gas is not used.

Using the selected parameters gets an excellent reproducibility of results in the thermograms. In addition, test times are adequate, due to that the average warming rates are higher than the  $3\text{ °C min}^{-1}$  for the studied temperature range.

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