Journal of Thermal Analysis and Calorimetry, Vol. 72 (2003) 1081–1086

A GENERAL INTRODUCTION TO SCTA AND TO RATE-CONTROLLED SCTA

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Introduction

Rate-controlled SCTA is part of the now broad ensemble which is called, since a previous workshop organized in 1996, during ICTAC 11, Sample Controlled Thermal Analysis or SCTA. Because of the many forms of SCTA which were devised, it seems useful to propose a general framework to make it easier to list and describe them. This is therefore what we shall do before considering more precisely the case of rate-controlled SCTA.

Keywords: rate-controlled SCTA, SCTA, temperature-controlled thermal analysis

A general framework for the SCTA family in the scope of thermal analysis

Thermal analysis in general can be said to embrace any method or technique able to record the value of a property (*X*) of a sample (*S*) *vs*. temperature (*T*), as shown in Fig. 1. The property can be any (mass, length, amount of gas evolved, heat exchanged, overheating…) provided it lends itself to a measurement.

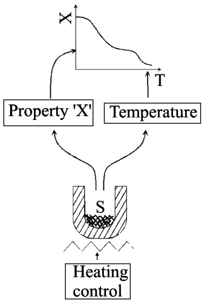

Fig. 1 General principle of thermal analysis

Now, there are two basically different ways to control the heating of the sample:

– One way, which is the most broadly used, consists in imposing a temperature programme selected by the experimenter (most often, with a linear heating which

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1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

lends itself to easier reproducibility and interpretation than more sophisticated temperature programmes); the heating control loop is therefore simply fed by temperature and time, as represented in Fig. 2. This leads to the broad family of temperature-controlled thermal analysis, which could also be called conventional thermal analysis since it is, nowadays, the most usual.

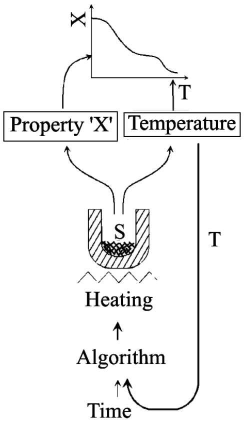

Fig. 2 Temperature-controlled TA (conventional TA)

- Another way, where the heating depends, partly or totally, on a feed-back from the sample itself; the use of this feed-back is the distinctive feature of sample-controlled thermal analysis (SCTA).

Here again, this SCTA family can be easily splitted into two main categories, depending on the more or less exclusive and permanent action of the feed-back upon the heating of the sample.

- It is indeed possible to exclusively control the heating of the sample after one or several properties (*X*) of the sample, associated with the measurement of time (*t*), as represented by the heating control loop in Fig. 3; this association of (*X*) with (*t*) finally involves, in a way or the other, the derivative, with respect to time, of the physical quantity measuring (*X*); since this derivative is a rate, itself directly related to the rate of transformation of the sample, one can speak here of solely rate-controlled SCTA (we must therefore keep in mind that the word rate will not be used, in the rest of this contribution, to designate a heating rate, like in conventional thermal analysis, but always a rate of transformation).

Now, it is also possible to use, as heating controlling parameters, not only (*X*) and (*t*), but also the temperature (*T*), as represented in Fig. 4; this opens the most recent form of SCTA which is therefore rate- and temperature-controlled SCTA.

Since each of the two basic forms of SCTA just mentioned can itself be split into two main sections, we arrive to the general framework presented in Table 1:

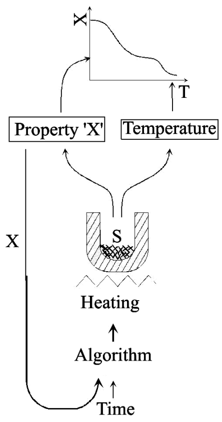

Fig. 3 Rate-controlled thermal analysis

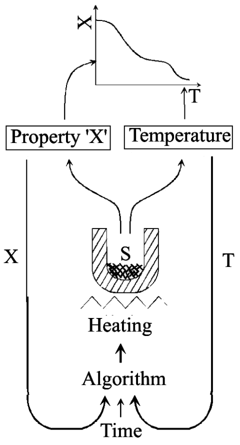

Fig. 4 Rate- and temperature controlled TA

Table 1 A general framework for the SCTA family: outline

A) Solely rate-controlled SCTA	B) Rate- and temperature-controlled SCTA
1) Constant rate TA	1) Alternate rate- and temperature-controlled
2) Varying rate TA	2) Combined rate and temperature-controlled

The four main forms of SCTA listed in Table 1 are not simply theoretical: they actually correspond to an experimental reality which was already explored. To give an idea, we list in Table 2 a number of milestones in these developments, with indication of the names first used by the authors and of the corresponding bibliographical reference.

Table 2 A general framework for the SCTA family: details

A) Solely rate-controlled SCTA	B) Rate- and temperature-controlled SCTA
1) Constant rate TA -Constant rate TA, first limited to evolved gas detection [1] -Constant rate TA (CRTA), generalized to the whole field of TA, whatever property is measured [2] -Quasi-isothermal, quasi-isobaric TG, first limited to thermogravimetry [3]	1) Alternate rate- and temperature-controlled -Stepwise isothermal analysis (SIA), with alternate linear heating and isothermal conditions confining rate of transformation between two limits [9] -Forced stepwise isothermal analysis, with experimental sub-division of main step, to derive kinetic parameters [10] -Max res, with combination of two heating rates
2) Varying rate TA -Rate-jump TA, with alternate imposition of two rates of transformation to derive assumptionless, isoconversional energies of activation [4] -Controlled decomposition rate TA (CRTA), when heating control is too loose to really keep the rate of transformation constant [5] -Increasing rate TA, for kinetic discriminations [6] -Modulated rate EGA [7], Modulated rate TG [8]	2) Combined rate- and temperature-controlled -Constrained TA [11] -High res TA [12] -Temperature-resolved SCTA, Time-resolved SCTA [13] -Dynamic heating -Constrained rate DSC [14, 15]

Solely rate-controlled SCTA

Let us now add a few comments to the left side of Table 2, which deals with solely rate-controlled SCTA.

The first category is that of constant rate TA. This is indeed the first type of SCTA control which came to the mind of researchers. It first started in the form of what we would call today constant rate evolved gas detection (CR-EGD), in Paris, where the experiment was set up [1] and of constant rate thermogravimetry (CR-TG), in Budapest, where a patent was filed and published [16], before the publication of the first experimental results [3]. Now, it took several years before it was realized that this was a quite general approach which could be applied with any type of thermal analysis instrument, by simply modifying the heating control loop, whatever physical quantity is monitored by the instrument (gas flow evolved from the sample, sample mass, heat exchanged by the sample etc…). This approach was then given the acronym of CRTA [2]. It was shown to be extremely efficient for the homogeneous and reproducible activation and outgassing of adsorbents (as will be developed in a further section of this workshop) and for the enhancement of the resolution of the thermal analysis recordings.

The second category is that of varying rate TA. There are actually two good reasons for varying the transformation rate in a SCTA experiment: either because one is not able to do otherwise (because of a loose control of the rate of transformation: for instance, when the control is based upon the measurement of the gas flow evolving from the sample and when the composition of the gas varies [5]) or because it is done on purpose, mainly in view of a kinetical analysis of the experiment [4, 6–8]. The main outcomes are then the possibility to determine an activation energy with no assumption on the mechanism and on any 'function of α' [4] and a very efficient way to discriminate between the main types of reaction mechanisms (involving a nucleation and a growth of nuclei, a diffusion, a geometrical contraction of the reacting interface…) simply after the general shape of the CRTA curve [17].

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