

Controlled rate evolved gas analysis: 35 years of rewarding services

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Abstract

This paper reviews, in a chronological way, not avoiding a personal touch, a number of aspects of controlled rate evolved gas analysis (CR-EGA): principle, practical (and fortuitous) reasons for its start, difficulties encountered, main developments and specific applications, especially in the field of finely divided or porous materials, including high resolution thermal analysis, preparation of Taylor-made porous adsorbents and kinetical studies. © 1997 Elsevier Science B.V.

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1. Introduction

This paper provides a survey of the start and development of controlled rate evolved gas analysis (CR-EGA) since the early 1960s. The principle of this thermo-analytical technique is given in Fig. 1: the heating of the sample does not follow any pre-determined temperature programme. Instead, it is carried out in such a way that the rate of evolution of the gas phase produced by the thermolysis is continuously kept at the desired value. This value is most often kept constant throughout the thermal analysis but it can also follow a pre-determined programme, like for instance, as we shall see, a modulation. Progressively [1,2] it was realized that this technique was part of the much broader method of controlled transformation rate thermal analysis (CRTA) which makes use of any physical property of the sample in order to control its rate of transformation through appropriate heating. Quite recently, at the 'CRTA Workshop' held during

the Tenth ICTAC Congress in Philadelphia, in August 1996, it was recognized that CRTA itself enters the broader scope of sample controlled thermal analysis (SCTA) which makes use of any feedback from the sample to control its heating; this includes cases where the rate of transformation is not pre-determined and is related, by a controlling algorithm, to a priori unknown events (especially taking place in the sample).

Since this paper is part of a very special volume, to which many good and old friends in the field of thermal analysis are contributing (although not all of them, unfortunately!), I found it appropriate to give it a more personal touch, and to analyse the succession of events which helped – or delayed – the development of this aspect of thermal analysis.

2. The need: Good control of a thermal decomposition

When I started my thesis work in the Sorbonne, in 1959, things in Paris were just starting to move

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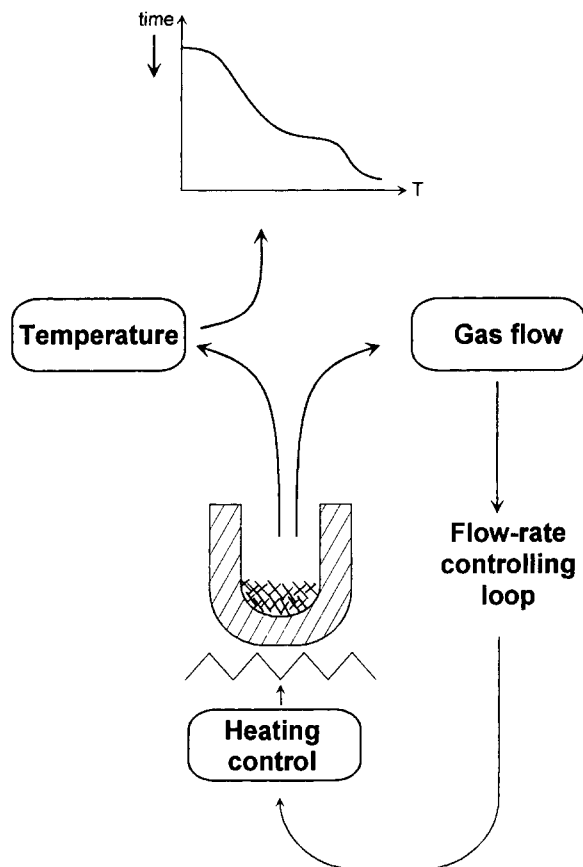


Fig. 1. Principle of controlled rate evolved gas analysis (CR-EGA).

quickly: there was still, but not for long, only one faculty of sciences which shared the Sorbonne building with the faculty of arts. The first commercial NMR equipment was just arriving, together with the first dual-grating IR spectrometers (replacing those with fragile NaCl prisms). I had to use these techniques, together with the hydrolysis of diborane by surface water, to study the state of water in porous oxides, alumina and beryllia. I was provided with the precursor hydroxides (gibbsite, $\text{Al}(\text{OH})_3$ and α -beryllium hydroxide $\text{Be}(\text{OH})_2$) and had simply “to heat them under vacuum, by successive temperature steps (8 h each) and study the sample at the end of each temperature plateau.” There was no temperature ramp control and each temperature plateau was reached with appreciable overshoot. A few things puzzled or even worried me. One was the curious observation that the ‘vacuum’ thermolysis of gibbsite usually gave rise,

after a while, to the condensation of water droplets visible in the glass tubing of the adsorption bulb (where the thermal decomposition took place) just at the exit from the furnace. It seemed we were quite far from the expected thermolysis under ‘secondary vacuum.’ Also, once a temperature of ca. 180°C was reached, gibbsite started ‘boiling’ gently – sometimes less gently – under the action of evolving water vapour. The problem was critical when a 10 g sample had to be prepared in an NMR probe tube (at that time, the sample tube for broad band solid NMR was ca. 12 mm wide and 10 cm high): the safest way to carry out the gibbsite thermolysis under ‘vacuum’ was to use a silica wool pad on top of the $80\ \mu\text{m}$ grain size hydroxide. How meaningful was the vacuum I was measuring on the ‘good side,’ i.e. in the vacuum manifold? Was it not a poor way to prepare samples to be looked at by so expensive and sophisticated techniques? The worst happened with beryllia.

Our micron size hydroxide powder was indeed losing more than one third of its mass, under vacuum, between 160 and 165°C . It was practically impossible to carry out the dehydration of, say, a few grams of this very thin and light powder, under vacuum even when the layer was only a few millimetres thick, without observing, at a stage, sometimes after hours of manually operated ultra-slow heating, a sudden spurting of the powder into the vacuum line. Now, beryllia powder was considered to be lethal, when breathed in suspension in air, for a concentration as low as $0.1\ \text{mg per m}^3$. When the spurting out of the white powder in the all-glass manifold occurred as I was in another room and was discovered by a colleague, I could hear the electrical bell ringing my code through the five-storied laboratory. I simply had to run to the experiment, stop it, close the stopcocks and then spend most of the next Saturday afternoon, with a powder mask, to carefully flood and clean all tubings with water and acetone. During this time-consuming but simple operation, I was free to think of a way to avoid all that trouble.

3. The luck: A well-thought, well-built, Pirani gauge.

Luck arrived in the form of an LKB Pirani gauge of excellent quality. Our boss had bought it to improve the fine adsorption experiments my wife (and already

closest co-worker) was carrying out. It was expensive (the price of our new small car) and it was worth carefully reading the directions for use. The great thing was an adjustable alarm switch. This was what I needed, not only to warn me that something wrong was happening in the manifold, but to stop the heating as soon as the flow of water vapour evolving from the sample exceeded a pre-set value. On the afternoon the gauge arrived it was mounted on our standard out-gassing unit: it was used to measure the vacuum just at the exit of the sample bulb and before the constriction provided by a vacuum stopcock whereas the signal supplied by the on-off temperature controller to the mercury switch was brought to pass through the alarm switch of the Pirani gauge. An experiment was launched with beryllium hydroxide and, by great fortune at that time, a chart recorder was available to record the temperature. The next morning was great: the experiment was still controlling the dehydration of beryllium hydroxide at such a rate that the sample neither 'boiled' nor spurted, whereas the wavy temperature recording seemed to be restricted, by the sample itself, around 165°C. This was, in spring 1961, our first CRTA experiment and recording.

4. The game: Improving the procedure in the 'pre-transistor' era

Now that it worked, some improvements were, of course, welcome. They are illustrated in Fig. 2. The all-glass vacuum manifold was equipped with constrictions so as to allow three different pumping rates with the same setting of the residual pressure. The latter was of course selected in the range of good sensitivity of the LKB Pirani gauge, i.e. between 0.02 and 5 mbar. The alarm switch of the gauge (which was actually activated at the same time as the automatic change of range and sensitivity of the gauge) was still used, but only to forbid using the signal from the gauge when in the wrong range. This signal was sent to an on-off galvanometric controller, feeding itself the coil of a mercury switch (not represented in Fig. 2). The heating control was still 'rustic': the temperature recording was wavy, and the depth of the waves changed drastically as the sample was progressively brought from room temperature to 1000°C. This was slightly improved by a device 'à la Dubout' (Dubout

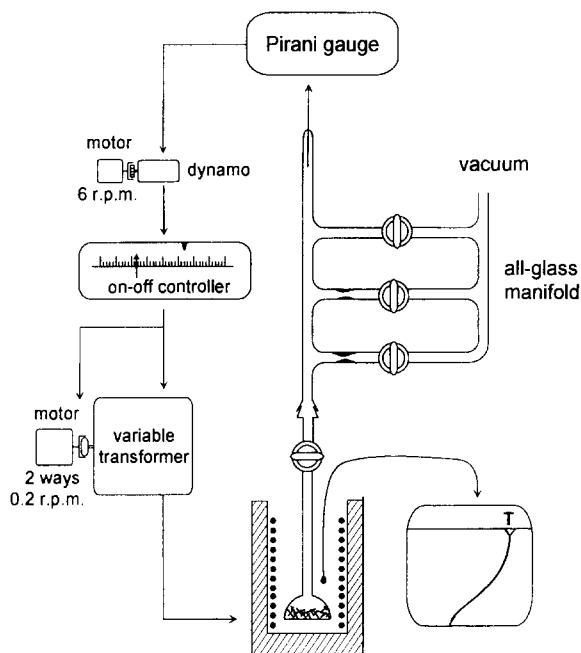


Fig. 2. An early form of CR-EGA used by the author between 1962 and 1966.

was at that time a famous cartoonist, native from Marseille, who liked complicated mechanisms with strings and pulleys) which used a variable transformer operated by means of a kind of long hand, a spring pulling this hand upwards, a bottle pulling the hand downwards (when filled with water), a rubber tube (allowing to empty the bottle, when left hanging down), an electrical coil (allowing to keep the tube, fitted with a small iron end, in the upper position) and an alarm switch on the temperature recorder: when a temperature of, say 400°C was reached, the current through the coil was switched off, the tube fell, the bottle was emptied, the string pulled up the hand, and the voltage delivered by the transformer increased from 60 to 120 V. The real improvement came when we introduced a device allowing to superimpose a roughly sinusoidal voltage to the signal from the gauge. This was first to oblige the galvanometric controller to operate much more frequently and to therefore limit the depth of the recorded temperature waves. But I was lucky: this sinusoidal voltage (which was simply obtained by means of a bicycle dynamo, operated by the electrical motor of a timer) provided the controller with a really proportional function,

whose band-width was adjusted with the help of a shunting resistance at the exit of the dynamo. Moreover, by fitting the variable transformer with a two-way electrical motor and by operating this motor in one direction when the mercury switch was on and in the other direction when it was off, the voltage was automatically adjusted in such a way that the heating and cooling periods were equal. This device now provided the heating control with an integral function. Being a chemist – not an electrical engineer – I lacked culture on these things. Very proud of this ‘invention,’ I discovered a few months later that the superimposition of a signal had been proposed by Gouy... at the end of last century, [3] and a few years later the operation of the variable transformer in the way reported above was the one used in the Mettler Thermoanalyser no. 1 which we purchased in 1968, so that it was probably already a conventional way to operate.

The important thing was that this CRTA set-up worked pretty well, and provided us with all the samples of alumina and beryllia we studied in our thesis work: mine was presented in 1964, and focused on the nature of the surface or internal water, whereas my wife’s, presented in 1965, focused on the study of the porous structure by physisorption of a number of gases. It was only in October 1963 that my boss allowed me to send a manuscript to the Bulletin de la Société Chimique de France: at that time, in France, a prerequisite for the thesis was for it to be an ‘original work’ and many professors considered that publishing prior to the presentation of the thesis weakened this originality. My boss did not want to co-author this paper. I think this was mainly by fairness, although he gave me another reason: “Rouquerol (the American, more friendly, habit of using the first name was not yet common in France), you know, a scientific reputation is slow to build up, but can be destroyed very quickly. So, if you don’t mind, I suggest that you publish alone.” So I did. [4].

5. The new toys: Automated systems, quadrupole analysis etc...

In the following decades, the limitation to the development and use of CR-EGA were, in great part, technical. For instance, the ‘modern’ assembly we built in 1967–1968, which is described and photo-

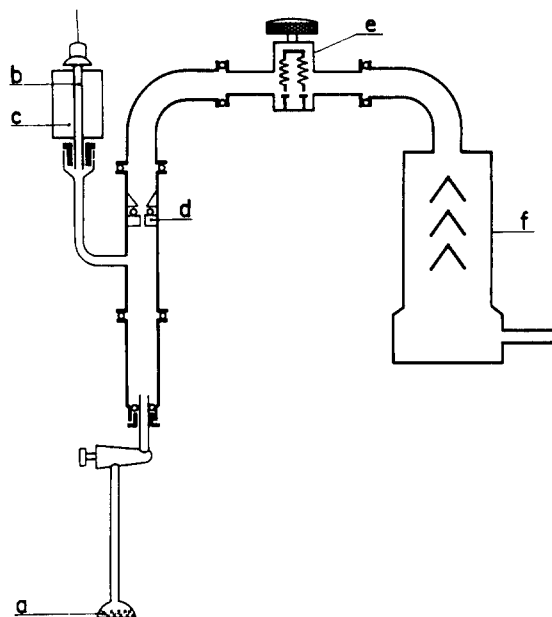


Fig. 3. All stainless-steel manifold for CR-EGA studies: (a) sample, (b) Pirani gauge, (c) thermostat to improve stability of gauge signal, (d) interchangeable diaphragm with calibrated hole, (e) bellow valve and (f) diffusion pump (from [1]).

graphed in a 1970 paper [1] and which was completely made of stainless-steel (cf. Fig. 3) was still, in great part, built in the laboratory, specially the electronic PID controller, which was not available in the market. It was at that time that we tried to figure out the sensitivity and resolution of the CR-EGA approach. For that purpose, we launched an experiment where, to lower the rate of gas evolution (and, therefore, the reaction rate) the usual constriction (a 1 mm bore hole through a 10 mm thick diaphragm) was replaced by a glass capillary coil, 0.5 mm bore and 1 m long. The CR-EGA of a 1 g calcite sample was then started. The experiment was carried out over 15 days. The observed mass loss corresponded to slightly less than 1/50 of the CO₂ content of the sample: 2 years would have been necessary to complete the experiment. The rate of gas evolution was less than 25 μg h⁻¹ and its control was still satisfactory (today we are using rates 2–3 times smaller for thermodesorption studies).

It was also at that time that we decided to operate a vacuum thermobalance in the CR-EGA mode: a Mettler Thermoanalyser was received in early June 1968 (just after our great general strike of May 1968) and immediately connected in the CR-EGA mode, so that,

in August, at the Second ICTA, (Worcester, MA) we could comment about three interesting features of this way of operation [5]: (i) the constant residual pressure kept unchanged the amount adsorbed on the mobile parts of this asymmetrical balance, (ii) the constant rate of gas evolution kept constant the reaction force on the crucible and (iii) the association of a control of the gas evolution with a recording of the mass change allowed detection of a change in the gas composition from a change in the slope of a mass recording. Incidentally, it was the gravimetric recording which finally convinced our former boss that, when one simple gas was produced, we were really able to carry out a thermolysis at a constant rate of reaction (which resulted in a straight line for the mass vs. time recording). This experiment was controlled by a Penning gauge (the residual pressure could be selected in the 10^{-5} to 10^{-3} mbar range) which simply had an on-off action on the programmer motor, so that we had stepwise heating, with minute steps [13].

In 1969, we wanted to control, if needed, the rate of production of one of the various gases produced by complex thermolysis. For that purpose, we bought a quadrupole analyser which was intended to be used in place of the Pirani gauge. Unfortunately, the signal of the quadrupole, when blocked on a pre-selected peak, badly lacked stability ($\pm 20\%$ quick variations were common) so that it could not be used to control the heating loop. We had to wait for an improvement of the quadrupole analysers before this experiment could be carried out, in the early 1980s, and applied to the thermolysis of kerogens [6]. Actually, it took one decade more (i.e. introduction of microprocessors in the control of the quadrupole) to really get the versatile equipment we wanted and to draw the benefit of all advantages of associating CR-EGA with a quadrupole [7]: (i) all gas evolved from the sample can be sent to the source of the quadrupole analyser (it is only a matter of selecting a satisfactorily low value for the controlled rate of reaction), (ii) therefore, there is no risk of discrimination of the gases after their molecular size, as it happens when a leak valve is used, (iii) there is no need of any carrier gas, no dilution of the gas evolved and therefore optimum sensitivity of the quadrupole analysis, and (iv) finally the enhanced separation of successive steps, which is a result of the CRTA mode, makes easier the interpretation of the quadrupole spectra.

Other interesting developments in CR-EGA were aimed at allowing experiments under atmospheric pressure, usually in the presence of an inert carrier gas. These were devised by Stacey [8] who studied the reduction of a catalyst by hydrogen, by Reading [9] who used the IR signal on the gas phase to control the reaction rate, or by Criado [10] who carried out a controlled oxidation. It is along these lines that we recently developed a CR-EGA apparatus using a high-sensitivity gas flowmeter based on the concept of a 'pneumatic Wheatstone bridge' [11]. This can be used to study any thermal reaction involving the adsorption or evolution of a gas (e.g. dehydration, a reduction by hydrogen) at rates as low as $1 \text{ cm}^3(\text{STP}) \text{ h}^{-1}$.

The study of water evolution from hydrates recently brought us to start the experiments at -100°C , with what we call a 'cryo-furnace' whereas the need to prepare or simply outgas samples in a highly reproducible way (especially for adsorption microcalorimetry experiments) or to carry out kinetical studies in a careful and slow manner brought us to build a family of relatively simple, though fully automated CR-EGA set-ups, collectively known in the laboratory as the 'clarinet,' where 10 independent experiments can be carried out at the same time.

6. The exotic fruits: Special thermal analysis, kinetics and products

We shall simply illustrate by a few examples the very special information brought by CR-EGA.

In *thermal analysis* proper, the separation of successive steps can be enhanced in a dramatic way by selecting the appropriate rate of reaction and residual pressure. A striking example is that of the thermolysis of hexahydrated uranyl nitrate, where standard TG, even at the relatively low heating rate of 1 K min^{-1} , is far from showing the stepwise decomposition obtained by CR-EGA (cf. Fig. 4) [12].

In the *study of kinetics*, one must often make a special effort to admit that the kinetics and mechanism can be reached even by a method which makes everything opposite to the conventional approach: instead of heating the sample after a pre-determined temperature programme and recording the resulting reaction rate, in CR-EGA one selects a reaction rate and measures the temperature requested by the sample to reach that

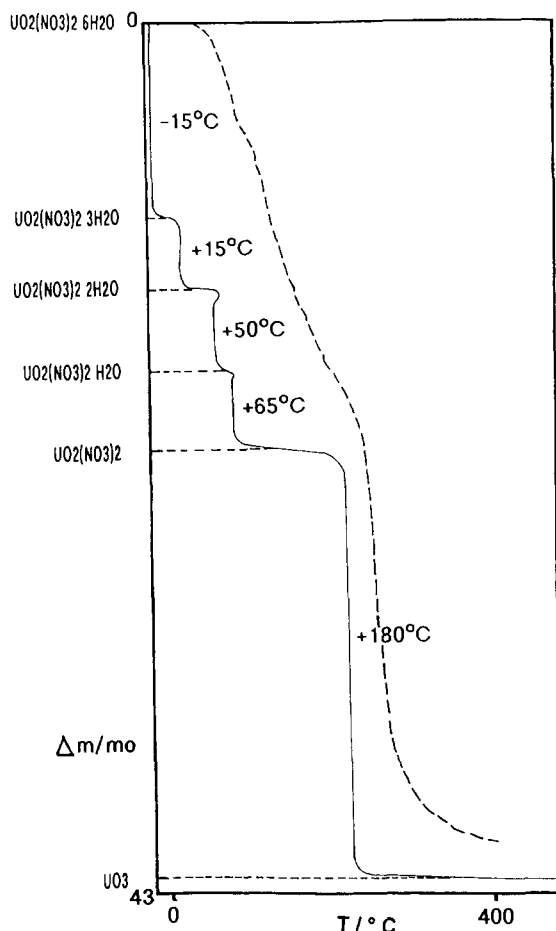


Fig. 4. Thermolysis of hexahydrated uranyl nitrate. Comparison of a TG trace (dashed line, obtained with flow of N_2 , 1 bar, at heating rate of 1 K min^{-1}) with a CR-EGA trace (plain line, left) obtained under constant pressure of $5 \cdot 10^{-2}$ mbar and constant rate of 2 mg h^{-1} for 1 g sample) (from [16]).

rate. The advantages are (i) that the reaction rate is measured with great accuracy, since it is constant and (ii) that the temperature measured is usually much more meaningful than in a standard thermal analysis experiments where the existence of appreciable temperature gradients makes the concept of a sample temperature quite doubtful. Modulating the reaction rate provides a means for a continuous kinetic analysis. An easy modulation can be obtained by periodical switching between two pre-determined rates (fixed, for instance, after the number of holes drilled in two diaphragms used one after the other). We call it the 'rate-jump' method [13]. Fig. 5 shows a set of 'rate-

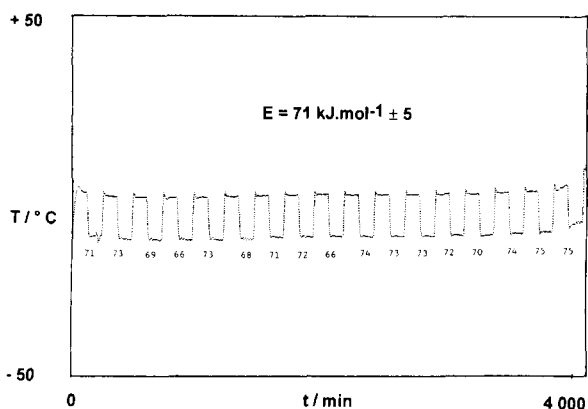


Fig. 5. Application of rate-jump method for the continuous determination of the activation energy: here, 17 independent measurements during the first step of dehydration of hexahydrated uranyl nitrate are presented (from [14]).

jump' measurements: 100 of them were carried out, successively, for the total thermolysis of hexahydrated uranyl nitrate, and confirmed the unique character of each of the 5 steps of this thermolysis [14].

In the *preparation* of new, highly homogeneous products, especially micro- or mesoporous, CR-EGA has often provided unexpected results: allowing for instance, to select and get a mono-disperse pore size in oxides like alumina or beryllia [15], or allowing to develop at will one or two types of pores in uranium oxide, and to unloosen at will the sheet-like structure of the parent nitrate [16], or even allowing to drill, also at will, either cylindrical or funnel-shaped pores in alumina crystals [17].

7. Conclusions: The preferred fields of application and development of CR-EGA

As we saw, CR-EGA originated with the study of fine powders; it is still in the field of porous solids and powders (to be used as adsorbents, reactive solids, pigments, ceramics etc.) that CR-EGA finds its privileged applications: *thermal analysis proper* (taking into account the importance of the desorption step whose control requests a control of the surrounding partial pressures), simple outgassing (in view of subsequent adsorption experiments carried out in the same bulb or in the same pan – in case of a vacuum microbalance), *thermal preparation or modification in*

highly reproducible conditions, and, *kinetical study* of the above transformations with a severe reduction of the experimental uncertainties (resulting from an appropriate reduction of thermal and gas composition gradients) and the great possibilities offered by the modulation of the rate reaction.

Nevertheless, the extreme sensitivity and resolution of this technique also prepares it for a broader field of application, especially when used with its most natural 'room-mate,' also fond of high vacuum, viz. the quadrupole analyser.

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