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# A NEW TYPE OF CRUCIBLE FOR TG AND DTA

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New types of crucibles for thermogravimetry and differential thermal analysis are described for use with conventional equipment, enabling extremely rapid movement of the gaseous species through the sample and sample holder. Its use in studies of oxidation or decomposition reactions is illustrated by considering the oxidation of $UO_2$ and the decomposition of $CaC_2O_4 \cdot H_2O$.

The influence of experimental variables such as the heating rate, sample size and crucible material on the TG and DTA curves and hence on the conclusions and deductions drawn therefrom have been discussed in previous publications from this laboratory [1–3] as well as from others [4, 5]. It is also known that in reactions involving a gaseous reactant or product, the restricted movement of the gaseous species in and around the sample and the sample holder may initially suppress the reaction rate to a considerable extent, but enhances the temperature at which the reaction is first detected as well as the peak temperature [4]. Free and rapid movement of the gaseous species is facilitated by using either very small amounts of the sample spread over a large area or polyplate type sample holders [6] or sample holders with porous bottom and cover plates [7]. Each of these suffer from one or more disadvantages such as requiring special high gain equipment of extreme sensitivity or fabricational difficulties.

The present note describes a sample holder which can be used with conventional equipment, yet enables extremely rapid movement of the gaseous species through the sample and the sample holder. Its use in studies of oxidation or decomposition reactions is illustrated by considering the oxidation of $UO_2$ and the decomposition of $CaC_2O_4 \cdot H_2O$.

## Wire-gauze sample holders

The sample holders (crucibles) for both TG and DTA are made from 80 mesh platinum wire gauze which is readily available. Suitably sized pieces of this wire gauze are cut and each piece is folded upon itself and gently tapped to reduce the pore openings and also to give rigidity to the platinum gauze. By this method, the mesh size is sufficiently reduced so that powders of 240 to 300 mesh

are retained, although it may not be able to retain a liquid phase of low viscosity. The TG crucible is shaped from a single piece of this material. In the DTA crucible except for the center thermocouple well, which is made from platinum as in our older design [8], the rest (the bottom and sides) is made of this gauze

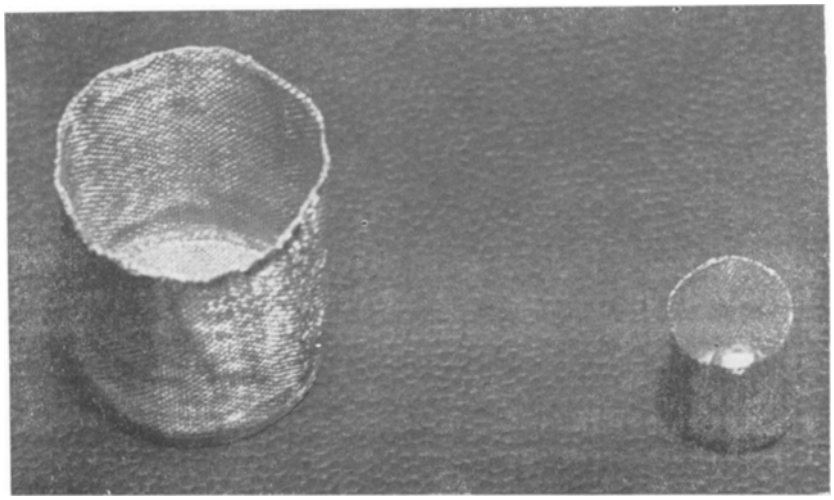

Fig. 1. Platinum wire gauze crucibles — (a) TG, (b) DTA

material. The dimensions of the new crucibles (TG: 1.9 cm dia, 2.3 cm height; DTA: 0.9 cm dia, 1.2 cm height) are identical with those of the normal crucibles used, and were chosen to fit the existing equipment. However, these could be suitably modified for equipment of other makes or design. The crucibles shown in Fig. 1 were fabricated to our design by M/s Ravindra Heraeus Ltd., Bombay.

## Experimental

*Materials used:* Calcium oxalate monohydrate $CaC_2O_4 \cdot H_2O$ was prepared as described earlier [2]. It was ground, sieved and the fraction between 240 and 300 mesh B.S.S. was used. 400 mg of this sample was taken for DTA runs.

Uranium oxide used was of nuclear purity (made by Atomic Fuels Division of the Bhabha Atomic Research Centre, Trombay, India). Because of general exposure, the composition when used was $UO_{2.07}$. The powder was ground, sieved and the fraction between 240 and 300 B.S.S. mesh was used. 2.50 g and 1.0 g of this sample were used for TG and DTA runs respectively.

Pure, previously calcined, alumina, $Al_2O_3$, was used as reference in DTA.

*Thermogravimetry:* Thermogravimetry was carried out on a Stanton recording thermobalance of 1 mg sensitivity in static air. The oxidation runs were also

made in flowing oxygen (flow rate: 0.47 litre/min.; flow direction: downwards) using cylinder oxygen gas.

*Differential thermal analysis:* The differential thermal analysis equipment was of our own design and used chromel-alumel thermocouples for measuring the differential e.m.f. and the sample temperature, and Pt vs Pt – 10% Rh thermocouple for furnace control. The differential e.m.f. and temperature were simultaneously recorded on a two pen recorder with a variable narrow span for recording the $\Delta T$ and a standard temperature range for recording temperature. The DTA curves were obtained in static air as well as in a stream of oxygen flowing under the same conditions as above.

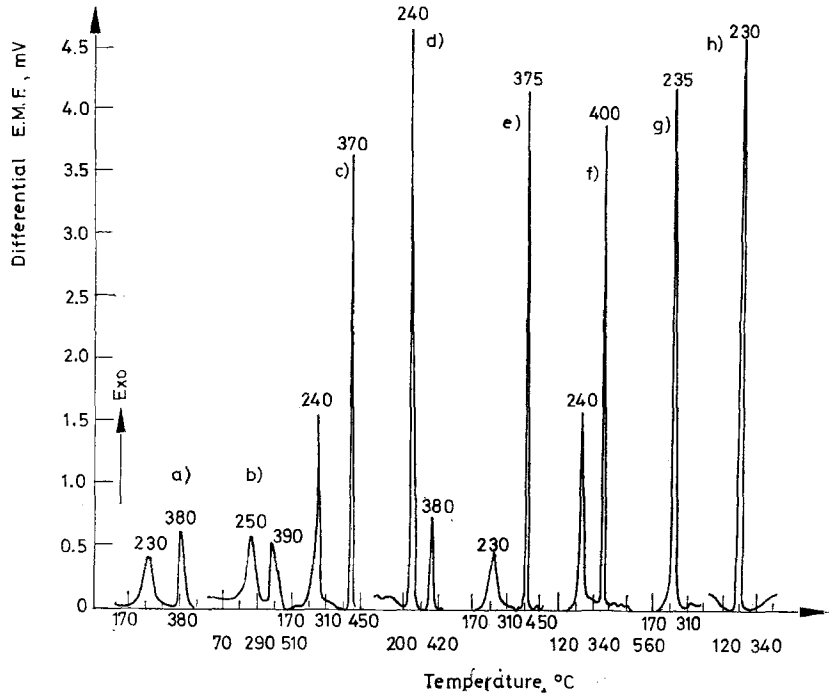


Fig. 2. DTA curves for the oxidation of $UO_2$

| Heating rate | 6°/min | | 10°/min | |
|---|---|---|---|---|
| Pt crucible | normal | gauze | normal | gauze |
| Static air | curve (a) | (c) | (b) | (d) |
| Flowing oxygen (0.47 l/min) | curve (e) | (g) | (f) | (h) |

## Results

### *Oxidation studies*

The DTA and TG curves for oxidation of $UO_2$ in normal crucibles and the platinum gauze crucibles are shown in Figs 2 and 3 respectively.

The oxidation of $UO_2$ is known [9] to proceed in two steps

$$UO_2 \xrightarrow[180^\circ]{} U_3O_7 \xrightarrow[360^\circ]{} U_3O_8$$

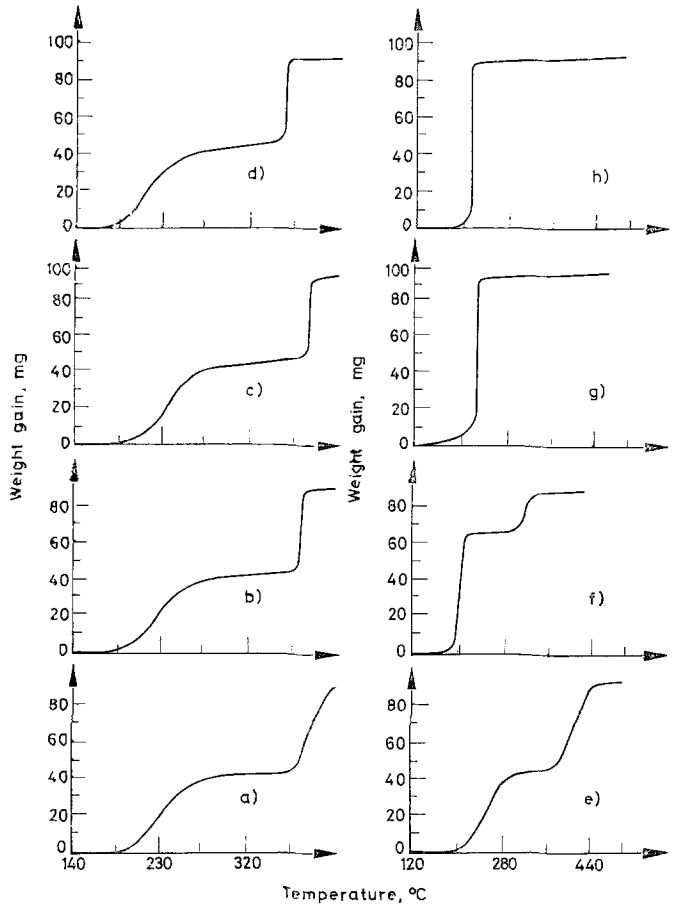


Fig. 3. TG curves for the oxidation of $UO_2$

| Heating rate | 4°/min | | 8°/min | |
|---|---|---|---|---|
| Pt crucible | normal | gauze | normal | gauze |
| Static air | curve (a) | (b) | (e) | (f) |
| Flowing oxygen (0.47 l/min) | curve (c) | (d) | (g) | (h) |

giving rise to two exothermic peaks in DTA and two steps in TG [10], with the first exotherm smaller than the second exotherm.

From Fig. 2 it can be seen that while initial and peak temperatures are lowered the peaks become extremely sharp and their intensity is enhanced considerably when wire gauze crucibles are used. When a faster heating rate (10°/min) is used (curve d, Fig. 2), the first peak due to oxidation to $U_3O_7$ is more intense. Further when the runs were taken in oxygen atmosphere (curves g and h, Fig. 2) there is only a single peak.

Similar enhancement of the oxidation reaction is also observed in the thermogravimetric experiment (Fig. 3). With a fast heating rate of 8°/min and using a wire gauze crucible in dynamic oxygen atmosphere the oxidation is found to proceed in a single step. With the heating rate of 8°/min in static air atmosphere using the wire gauze crucible, the first intermediate plateau is observed to correspond to as high as $UO_{2.5}$ as against $UO_{2.34}$ found with normal crucibles. This

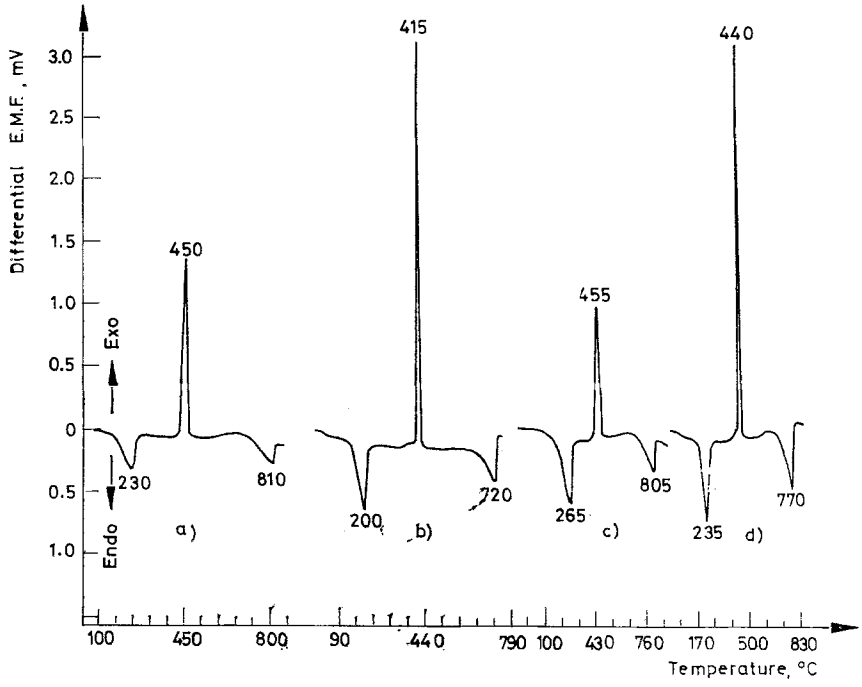


Fig. 4. DTA curves for the decomposition of $CaC_2O_4 \cdot H_2O$

| Heating rate | 6°/min | | 10°/min | |
|---|---|---|---|---|
| Pt crucible Static air | normal curve (a) | gauze (b) | normal (c) | gauze (d) |

shows that if the initial oxidation to $U_3O_7$ is very rapid and the entire mass gets oxidized almost simultaneously, the heat generated in that relatively short duration is adequate to locally raise the temperature of the sample so that the next reaction $U_3O_7 + \frac{1}{2} O_2 \rightarrow U_3O_8$ takes over. The extent to which the second reaction occurs almost simultaneously will depend upon the local rise in temperature and the ready availability of oxygen. Hence in static air, only the material near the wall gets oxidized to $U_3O_8$ giving an average composition of $UO_{2.5}$ in TG and an enhanced peak in DTA. That there is sufficient local heating produced has been seen in the sharp rise in sample temperature.

The reaction process can thus be considerably enhanced (altered) when the availability of oxygen is increased by the use of the wire gauze crucibles.

*Decomposition reaction*

The decomposition of $CaC_2O_4 \cdot H_2O$ was studied with both types of crucibles. Similar enhancement in the reaction is observed but this is much more pronounced in DTA than in TG. It can be seen from Fig. 4 that, as in the case of oxidation, the DTA peaks are considerably sharpened and also the initial and peak temperatures are considerably lowered when the wire gauze crucibles are used. The wire gauze crucibles allow the gaseous products to escape out of the sample bulk very readily. Thus there is very little, if any, pressure build up within the sample to suppress the decomposition reaction and the reaction takes place at a temperature more close to the true decomposition temperature. The exotherm which is due to the oxidation of the liberated CO in the air environment of the furnace, is also made extremely sharp.

## Conclusion

It is thus evident that the use of the wire gauze crucibles for reactions involving a gaseous component either as a product or a reactant is extremely advantageous. Further, since the peaks become extremely sharp it is easier to determine the peak temperatures much more precisely.

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RÉSUMÉ — On décrit un nouveau type de creuset pour la thermogravimétrie et pour l'analyse thermique différentielle, adaptable aux dispositifs usuels et permettant un passage extrêmement rapide des gaz à travers l'échantillon et le support d'échantillon. L'exemple de l'oxydation de $UO_2$ et de la décomposition de $CaC_2O_4 \cdot H_2O$ illustre son application à l'étude des réactions d'oxydation ou de décomposition.

ZUSAMMENFASSUNG — Neuartige Tiegel werden zur Thermogravimetrie und Differentialthermoanalyse vorgeschlagen, die in den üblichen Einrichtungen benützt werden können. Sie ermöglichen eine extrem schnelle Bewegung der gasförmigen Produkte durch die Probe und den Probenhalter. Ihr Gebrauch zur Untersuchung von Oxydations- und Zersetzungsreaktionen ist am Beispiel der Oxydation von $UO_2$ und der Zersetzung von $CaC_2O_4 \cdot H_2O$ illustriert worden.

Резюме. — Описан тигель нового типа для термогравиметрии и дифференциального термического анализа. Применение этого тигля дает возможность пользоваться конвенционным прибором и при изучении превращений возможно очень быстрое движение различных газов через образец и держатель. Использование тигля при изучении реакции окисления или распада проиллюстрировано на примере окисления $O_2$ и распада $CaC_2O_4H_2O$.