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Dedicated to Professor Dr. H. J. Seifert on the occasion of his 60th birthday

AN ACCURATE AND COMPACT HIGH–PRESSURE THERMOGRAVIMETRIC ANALYSER

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The design and operation of a bench-top high-pressure thermogravimetric analyser is described and illustrated. It has the following specifications: sample mass 1-100 mg; temperature range 25-700°; heating rate 0.1-10 deg/min; pressure range 0-50 bar of air, O_2, N_2, CO_2, CO or H_2. Mass and temperature are measured with a maximum error of 0.1 mg and 5 K for any conditions of pressure, temperature and heating rate. The instrument can be used to study substances under industrially realistic conditions of pressure and temperature and to perform high-pressure accelerated oxidation tests on lubricants and polymers. In these areas of application, the instrument offers a new standard of accuracy and ease of use which make it comparable to commercially available high-pressure DSC systems.

Most applications of high-pressure thermogravimetry (HP–TG) fall into two categories: the measurement of gas sorption for solids, and the study of solids under industrially realistic conditions of temperature and pressure. High–pressure thermogravimetric analysers (HP–TGAs) for sorption studies are well-established and are optimised for large sample masses and isothermal operation, usually below 200°. HP–TGAs have also been described in the literature for studies which simulate industrial conditions for such processes as coal gasification and gas desulphurisation [1-3]. However, almost all of these instruments operate isothermally and are less accurate, less easy to use and more bulky than normal TGAs. In contrast to TGAs, high-pressure and normal differential scanning calorimeters are not significantly different in these respects.

The aim of the development described here was to provide a HP–TGA with versatility in temperature programming, accuracy, ease of use, and size

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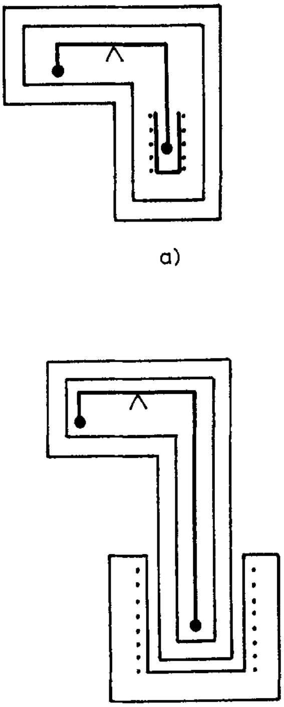
comparable to a normal TG for our intended applications. The following areas were of most interest: (a) activation, poisoning and regeneration of catalysts; (b) decomposition and polymerisation reactions; (c) oxidation of lubricating oils. Here the relevant experimental conditions fall in the ranges 20-700° and 0-50 bar with gases such as N_2, O_2, CO_2, CO, CH_4, and H_2.

Design considerations

Two configurations are possible for a HP–TGA as shown in Fig. 1: (a) a small furnace may be enclosed in a pressure vessel, or (b) the pressure vessel may be inside a larger furnace. Option (a) is used in commercial HP–DSCs and has the great advantage that the relatively low heat capacity and high heat loss of the furnace allow for accurate temperature programming. For these reasons it was the preferred configuration.


a)

b)

Fig. 1 Two configurations for a high-pressure thermogravimetric analyser (HP–TGA)

Both configurations in Fig. 1 can be arranged with a single furnace as shown or symmetrically. The symmetrical arrangement should lead to the cancellation of the effects of buoyancy and gas flow on the mass readings but requires the duplication of every item except the microbalance. Alternatively, with a computer to collect the data from a single-furnace system, the effects of buoyancy and gas flow can be removed by subtracting data for a blank run. This latter was the preferred option for economy of space and cost.

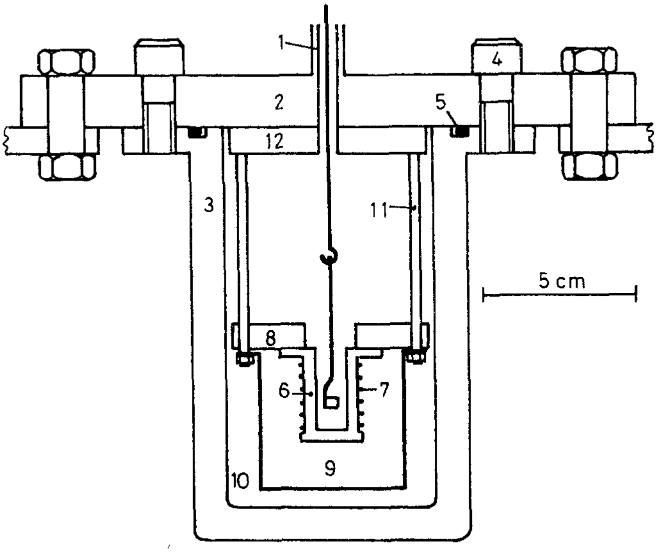


Fig. 2 The pressure vessel of the HP-TGA. The parts are described in the text

The next problem was that of deciding how to overcome the effects of convection currents. These currents develop in a fluid where there is a temperature gradient and they are particularly severe at high pressures. Their effect is to create fluctuations in the mass readings and sample temperature. The remedy is to minimize the temperature gradients and restrict the vertical flow of gas. As will be explained below, the novel furnace design used here achieves these results. Another feature of this design is that the furnace is fixed in position, so there is no need for a mechanism to raise and lower it.

The apparatus

The instrument is based on a Sartorius GmbH S3D–P high-pressure microbalance with a measurement range of 0-110 mg and a resolution of 0.001 mg. The control unit has an RS232 interface which sends readings to the data logger. This microbalance was supplied with its own pressure housing (rated 150 bar) and joins to the pressure vessel in Fig. 2 via the vertical tube (1). The pressure vessel in Fig. 2 comprises a top section (2) and a bottom section (3) held together by finger-tight bolts (4) and sealed by a pressure-sealing o-ring (5). The top section is bolted to a 450 mm-high, 250 mm–deep, 500 mm–wide frame which also supports the microbalance pressure housing. The vessel was certified for operation to 50 bar at 650°, although in practice the temperature of the vessel never exceeds 80°.

The furnace (6), which is shown in more detail in Fig. 3, is made of Inconel and has an internal diameter of 10 mm and an internal height of 30 mm. It is heated by a 100 Watt Nichrome resistance winding (7) insulated electrically from the furnace (6) by silica tape and surrounded by alumina

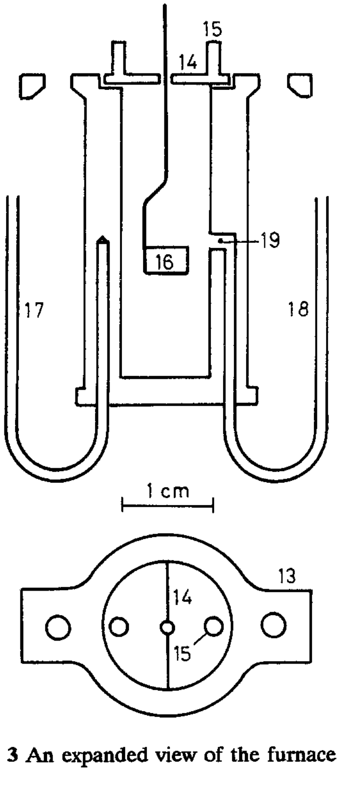


Fig. 3 An expanded view of the furnace

cement. The furnace is attached to a 10 mm-thick disc of insulation board (8) and surrounded by alumina insulation wool (9) contained in a metal cup (10). The whole assembly is suspended from the top of the pressure vessel by two 5 mm–diameter, 55 mm–long rods (11). The inside of the top of the pressure vessel is additionally shielded from heat from the furnace by insulating board (12).

One aim of the furnace design was to minimize heat transfer to the pressure vessel by: minimizing the exposed area of furnace (only the lid is exposed); providing adequate insulation; and minimizing direct thermal contacts (the only paths are through the rods (11)).

Figure 2 does not show the five fittings in the top of the pressure vessel for gas inlet, gas outlet, thermocouple, and two AC power leads. These fittings are standard compression glands which are widely available.

Figure 3 shows a section and top view of the furnace (heater omitted) in more detail. The two projections (13) are the points of attachment to the disc of insulating board (8). The furnace lid comprises two half–discs (14) with projecting rods (15) for manipulating them into position with the sample pan in position as shown. This manipulation is easily done using a pair of tweezers with tips specially bent down at a right angle. The lid fits into a recess at the top of the furnace to ensure easy assembly and good thermal contact. The overall effect of the lid is to improve temperature uniformity and to act as a barrier to vertical convection currents. The result is a noise level of only 0.05 mg under the worst conditions.

The sample is contained in a 6 mm–o.d., 4 mm–high Pt13%Rh pan (16) welded to a 0.5 mm–diam. Pt13%Rh wire. This assembly hooks onto the microbalance suspension wire and is readily positioned into or removed from the furnace by tweezers.

Figure 3 also shows how the 2 mm–o.d. Inconel–sheathed mineral–insulated thermocouple (17) fits into a well in the furnace wall and how the 0.0625 inch gas–outlet tube (18) receives gas from the furnace at outlet (19). The thermocouple is linked to the temperature programmer and from this an RS232 interface sends the sample temperature readings to the data logger. The sample temperature is calculated from the furnace wall temperature using data from a Curie point calibration experiment as explained below. The furnace temperature is controlled by a PID programmer.

Gas flow arrangement

If the atmosphere of interest is not air, the vessel is usually evacuated by a two–stage rotary pump to a pressure of 1 Pa before filling the apparatus through the top of the vessel (not through the furnace, otherwise the sample can be blown away). Once filled, a system of valves (not shown) is configured for either static or flowing operation. For a static atmosphere, the vessel is in effect connected to a cylinder with a regulator which sets the desired pressure. However, to avoid a pressure rise during heating, there is a controlled bleed of approx. 200 ml/min from a needle valve near the regulator. For an atmosphere to flow down the furnace, the arrangement is the same except that a needle valve at the end of tube (18) is opened to bleed gas to the atmosphere, typically 100 ml/min at STP.

Data collection and processing

Mass and temperature readings are usually logged each 6 s using a BASIC programme on a personal computer. At the end of the run, the data file is processed to correct the mass and temperature readings as described below, and the corrected data are plotted as shown in Figs 4-6 by customized software with a separate printout of the time, temperature, mass and first derivative (dy / dx) for the annotated points. This software allows considerable flexibility in smoothing the data and calculating the first derivative. Typically, the mass reading is smoothed over five points and the derivative at each point is calculated as the slope of the best-fit line through the five previous and five following points.

Corrections

Temperature readings

The only temperature recorded is that of the furnace wall, and the sample temperature is calculated from this by using the data from a Curie point calibration experiment under identical conditions of heating rate, pressure, and, ideally, gas type. Experimentally, Curie point measurements present no problem: a strong magnet is placed below the pressure vessel, and the mild steel of the vessel concentrates rather than diminishes the field. As an example of the type of results obtained, a calibration with a pressure of 35 bar static N_2 and a heating rate of 10 deg/min in the range 30-650^o gave the following values for $T_{\mathbf{furnace}} - T_{\mathbf{sample}}$: +10 K at 150^o, +28 K at 350^o, +30 K at 600^o. In most cases the correction corresponding to the

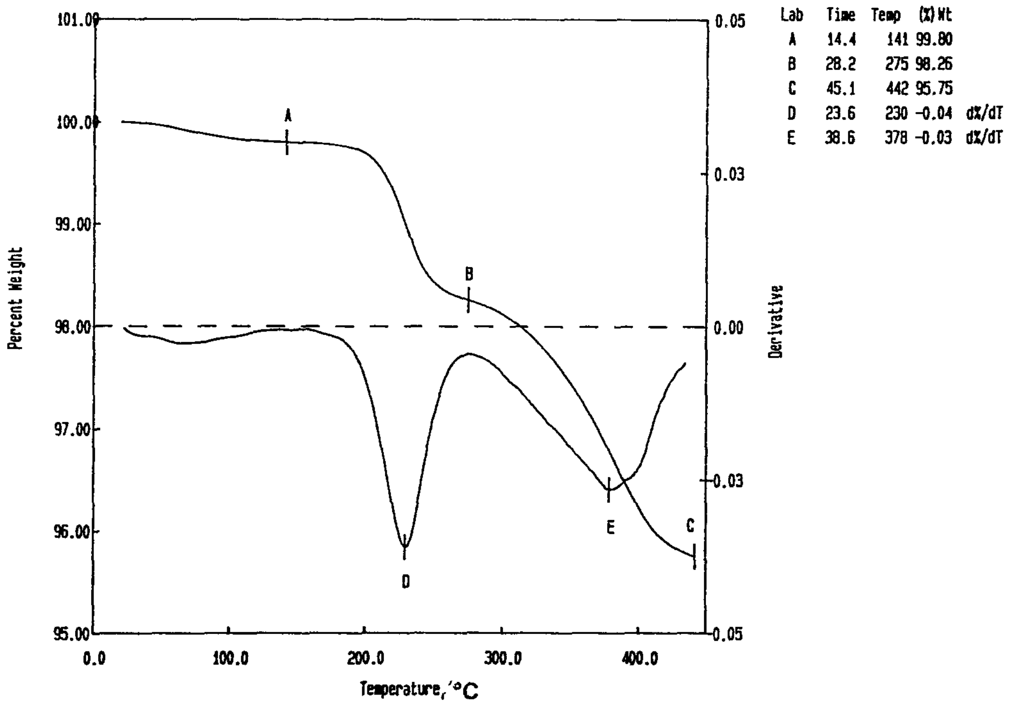


Fig. 4 The activation of a mixed oxide catalyst. Conditions: 50 mg; 30 bar H_2, 100 ml/min at STP; 10 deg/min

temperature range of interest is made to the data file, although a temperature-dependent correction procedure is possible using a BASIC programme.

Mass readings

The mass readings are corrected for buoyancy, gas flow, and any other effects by subtracting data for a blank run with identical conditions of pressure, gas type, heating rate, and with a similar volume of sample. Such blank runs are repeatable to within ±0.05 mg or better over a period of weeks. In the case of an inert gas, buoyancy and flow effects dictate the shape of the blank curve, and the magnitude of the effects increases with the density of the gas. However. with H_2, which one would expect to give an insignificant effect on the basis of density, there is a complication: H_2 dissolves in the Pt–Rh sample pan assembly during pressurisation and is evolved when the furnace is heated. For example, when the empty pan was heated in 20 bar static H_2 at 10 deg/min from 30 to 450°, the mass reading fell by 0.05 mg. On cooling, the H_2 was re-absorbed and the mass returned to its original value. This effect is of course easily cancelled by a blank subtraction, so accurate TG in H_2 presents no problems.

Another atmosphere of interest is CO for studies of catalysts in mixtures like syn–gas ($CO + H_2$). With CO there is the possibility of coke deposition at higher temperatures and pressures, so it was important to see if coke would deposit on the Pt–Rh sample pan assembly. Examination and weighing of the assembly after a blank run in 20 bar static CO to 500° showed that no carbon had deposited, so TG in CO is as accurate as in N_2. Some carbon did deposit on the Inconel furnace, as expected, but this was readily removed by heating to 650° in O_2.

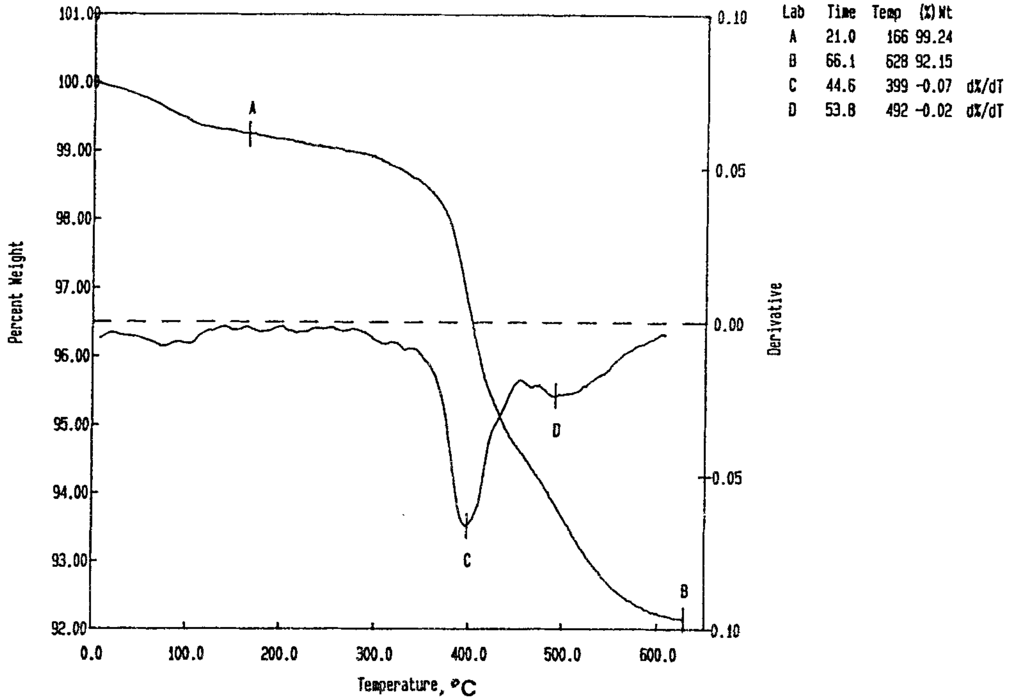
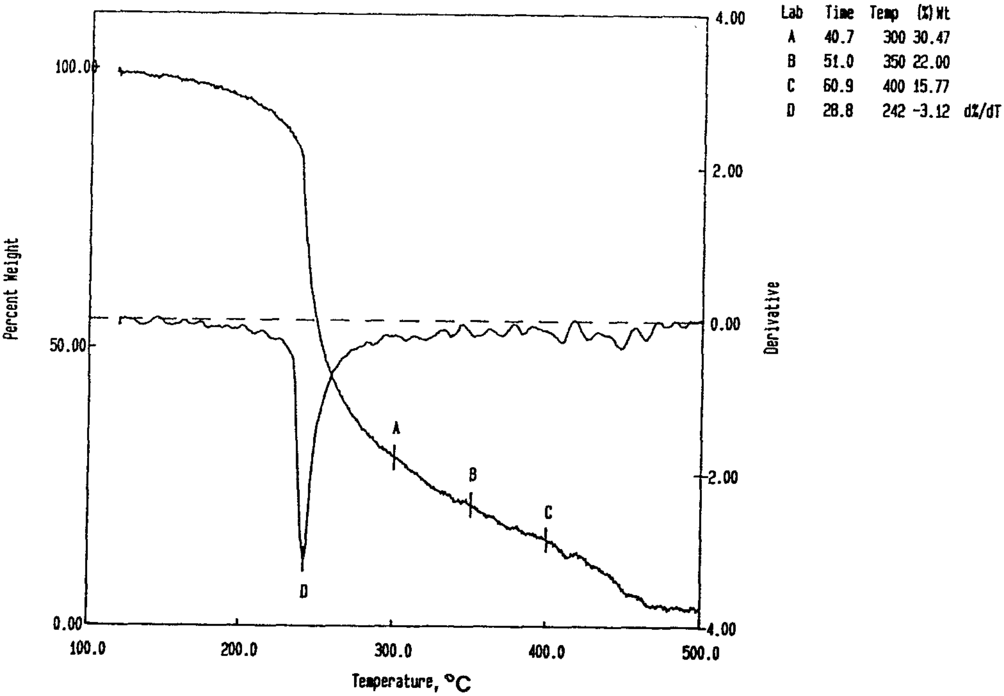


Fig. 5 The regeneration of a coked catalyst. Conditions: 28 mg; 30 bar 1% O_2 in N_2, 100 ml/min at STP; 10 deg/min

Examples

As mentioned, a major area of application for HP–TG is in monitoring the activation and regeneration of catalysts under realistic industrial conditions. Figure 4 shows the mass changes when a mixed-oxide catalyst is activated by heating in H_2 at 30 bar. The two stages of reduction, at 230° and 380°, are clearly resolved in the first derivative curve. Figure 5 shows the TG curve for the regeneration of a coked catalyst in 1% O_2 in N_2 at 30 bar. Again the first derivative curve resolves the two steps in the process, at 400° and 490°, corresponding to the oxidation of two types of coke.

The most demanding application planned for the HP–TGA was to monitor the oxidation of lubricating oils with a view to measuring the oxidation induction time or temperature and the remaining mass at various times or temperatures; these parameters can provide an indication of the likely performance of the oil in an engine. While induction times or temperatures can be readily measured by HP–DSC [4], HP-TG has not been applied in this area because no more than a few mg of sample can be used (more will ignite rather than undergo a controlled oxidation) and existing HP–TGAs are too inaccurate with such low masses. Figure 6 shows the TG curve for 1.0 mg of lubricating oil heated in air at 30 bar. The onset of oxidation is clear from the first derivative, and the residual mass can be read by point annotations on the TG curve.



Lab	Time	Temp	(%)Wt	
A	40.7	300	30.47	
B	51.0	350	22.00	
C	60.9	400	15.77	
D	28.8	242	-3.12	d%/dT

Fig. 6 The oxidation of a lubricating oil. Conditions: 1 mg; 30 bar air, static; 5 deg/min

Conclusions

(a) The apparatus for HP–TG described and illustrated here represents an important advance in accuracy and ease of use.

(b) The most significant feature is the ability to programme the temperature accurately. This mode of operation is much more convenient than running a series of isothermal experiments.

(c) These capabilities, together with the ability to operate in gases like H_2 and CO, open up new possibilities for accurate HP–TG studies of materials such as catalysts.

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Zusammenfassung — Bau und Funktion eines Hochdruck-TG-Analysators mit folgenden Spezifikationen wurden beschrieben: Probenmasse 1-100 mg; Temperaturbereich 25-700°C; Aufheizgeschwindigkeit 0.1-10 K/min; Druckbereich 0-50 bar für Luft, Sauerstoff, Stickstoff, Kohlendioxid, Kohlenmonoxid oder Wasserstoff. Die Meßgenauigkeit für Massen- bzw. Temperaturangaben beträgt 0.1 mg bzw. 5 K für alle Drücke, Temperaturen und Aufheizgeschwindigkeiten. Mit diesem Gerät können an Schmierstoffen und Polymeren unter Industriebedingungen für Druck und Temperatur Untersuchungen und hochdruckbeschleunigte Oxidationstests durchgeführt werden. Auf diesem Anwendungsgebiet ist das Gerät vollkommen vergleichbar mit kommerziell erhältlichen Hochdruck-DSC-Systemen.